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Coal-Fired Power Plant Ash Utilization in the TVA Region

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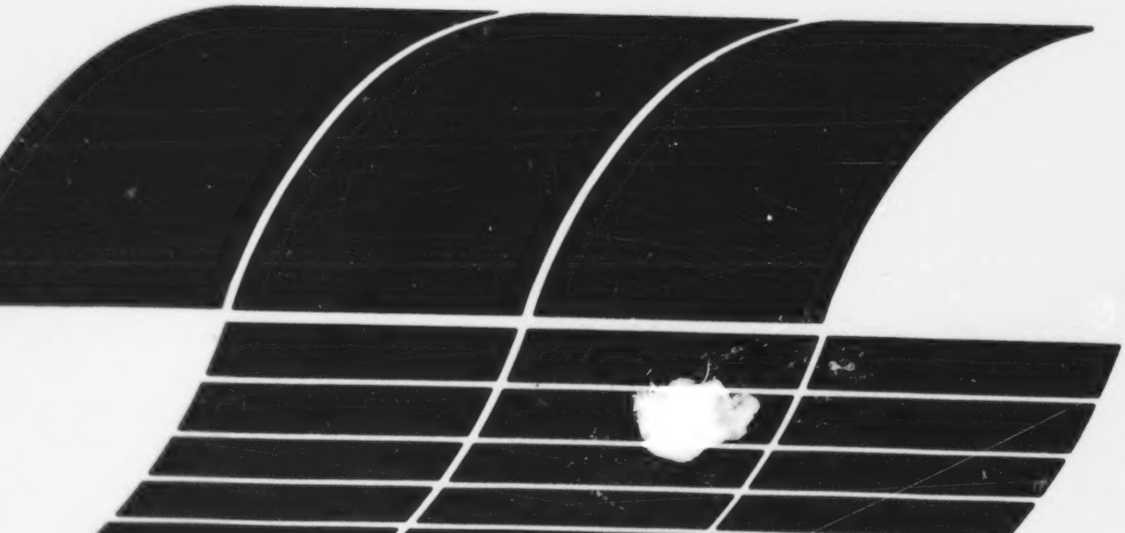

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16. ABSTRACT The report gives results of a study: (1) to summarize (a) production of coal ash nationally and by TVA's 12 major ash-producing steam/electric power plants, and (b) the physical/chemical characteristics of coal ash that affect ash disposal and/or use; (2) to review reported methods of coal ash use, emphasizing potential markets in the TVA system; and (3) to recommend potential R and D for coal ash use in the TVA system. Uses discussed include: concrete mixtures, mineral and magnetite recovery, lightweight aggregate, wastewater treatment, sanitary landfill liners, cenosphere reuse, agriculture, mineral wool insulation, and bituminous paving mixtures. The TVA region's predominant historical use of fly ash has been as a concrete additive; however, extensive pilot scale development is underway to advance ash use in the TVA region in such areas as mineral and magnetite recovery, and mineral wool insulation. Recommended studies include: (1) the feasibility of converting existing wet fly ash collection systems to dry collection and storage; (2) mechanical properties of ash to learn how to separate nonfloating cenospheres from ash; (3) other mineral recovery process choices (in addition to the one with Mineral Gas Co.); and (4) the potential uses, markets, generation points, transportation, and feasibility of extensive coal ash utilization in the TVA area.

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DISCLAIMER

This report was prepared by the Department of Civil Engineering of the University of Tennessee under a contract with the Tennessee Valley Authority (TVA), and has been reviewed by the Emissions/Effluent Technology Branch of the Utilities and Industrial Power Division of the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views or policies of TVA or the U.S. Environmental Protection Agency, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use. TVA makes no warranty or representation, expressed or implied, concerning the accuracy or usefulness of the information contained in the report.

ABSTRACT

The objectives of this study were to: (1) summarize the overall national production of coal ash; (2) summarize the production of coal ash within the Tennessee Valley Authority (TVA) power plant system consisting of 12 major ash-producing steam-electric power plants; (3) summarize the physical/chemical characteristics of coal ash as they affect the potential disposal and/or utilization of ash; (4) review and summarize existing literature on the utilization of coal ash with specific emphasis on areas which might be marketable within the TVA system for TVA coal ash; and (5) make recommendations on the potential future research and development needs within the TVA system for utilization of coal ash.

Topics covered included utilization in concrete mixtures, mineral recovery, magnetite recovery, lightweight aggregate, utilization of fly ash in wastewater treatment, utilization as a sanitary landfill liner, cenosphere reuse, agricultural uses, mineral wool insulation, and use in bituminous paving mixtures.

Specific data included in this report, relative to the production and utilization of coal ash in the TVA system, were collected by a combination of: (1) on-site visits to major power plants with active flyash utilization programs; (2) TVA data files; and (3) discussions with personnel responsible for various programs. Data reported on studies outside of the TVA system were obtained extensively through a literature search and review.

The predominant historical use of fly ash in the TVA region has been as concrete additives. However, extensive pilot-scale development efforts are being made to advance ash utilization in the TVA region in such areas as mineral recovery, magnetite recovery, and mineral wool insulation.

As a result of conducting this study, the authors recommend that the following studies also be conducted:

1. Conduct a feasibility study of the conversion of existing wet fly ash collection systems to dry collection and storage. This would lead to better fly ash utilization options within the TVA system.

2. Since some cenospheres do not float, study the mechanical properties of ash to learn how to separate nonfloating cenospheres from ash.

3. Conduct a study comparing other process choices and options to see if a preferred process, if any exists for the TVA region.

4. Conduct an integrated TVA area-wide market study for the potential uses, markets, generation points, transportation, and feasibility of extensive coal ash utilization.

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CONVERSION TABLE

A list of conversion factors for British units used in this report is as follows:

British	Metric
1 inch	2.54 centimeters
1 foot	.3048 meters
1 mile	1.609 kilometers
1 cubic yard	.76456 cubic meters
1 pound	.454 kilograms
1 ton (short)	.9072 metric tons
1 gallon	3.785 liters
1 part per million	1 milligram per liter (equivalent)
1 part per billion	.001 milligram per liter (equivalent)
1 British Thermal Unit per pound	2.325 Joules per gram

Section 1

INTRODUCTION

PURPOSE AND SCOPE

The passage of local, state, and Federal emissions regulations has resulted in the collection of significant quantities of coal ash which were historically emitted to the atmospheric environment. Subsequent passage of the Federal Water Pollution Control Act of 1972, and the Resources Conservation and Recovery Act of 1976, has placed additional requirements on the disposal of coal ash collected because of the chemical/physical characteristics of the various ashes. There has been an increasing interest in the potential utilization of ash due to the increases in total power production and increasing concern over the environmental impacts of such disposal.

U.S. ASH PRODUCTION RATE

The collection and disposal of coal ash (consisting of fly ash, bottom ash, and boiler slag) has become a problem of increasing concern in the past two decades. This concern has been amplified due to (1) the increased concern over the environmental impact of the disposal ash, and (2) the increase in total amount of ash generated.

Based on a survey conducted by the National Ash Association (NAA) in 1977 and presented at the Fifth International Ash Utilization Symposium of NAA in 1979,[33] it was estimated that there were 67.9 million tons of coal ash collected in 1977. Approximately 21% of this ash was utilized for purposes other than disposal. Table 1[33] summarizes the U.S. collection and utilization of coal ash from 1966 to 1977 and illustrates the significant increase in both production and utilization with time.

NAA has further projected that by the year 1985, the production rate will be 90 million tons/year with a utilization rate of 40%.[33] By the year 1990, it was estimated that the production rate would be 125 million tons/year with a 50% utilization.

TVA COAL ASH PRODUCTION

TVA depends upon coal-fired generating plants to produce approximately 80% of its total electrical generating capacity. These 12 steam plants consume approximately 35 million tons of coal per year and produce 5.6 million tons of coal ash.

Table 1: COMPARATIVE ASH COLLECTION AND UTILIZATION IN THE U. S. - 1966 to 1977

	Ash Collected in Millions of Tons				Ash Utilized in Millions of Tons				Ash Utilization in Percent			
Year	Fly Ash	Bottom Ash	Boiler Slag	Total Ash	Fly Ash	Bottom Ash	Boiler Slag	Total Ash	Fly Ash	Bottom Ash	Boiler Slag	Total
1966[a]	17.1	8.1	-	25.2	1.4	1.7	-	3.1	7.9	21.0	-	12.1
1967	18.4	9.1	-	27.5	1.4	2.3	-	3.7	8.2	25.0	-	13.5
1968	19.8	7.3	2.6	29.6	1.9	1.8	1.5	5.2	9.6	25.0	57.8	17.6
1969	21.1	7.6	2.9	31.7	1.9	2.0	1.0	4.9	9.1	25.6	33.0	15.3
1970	26.5	9.9	2.8	39.2	2.2	1.8	1.1	5.1	8.1	18.6	39.1	13.0
1971	27.8	10.1	5.0	42.8	3.3	1.6	3.7	8.6	11.7	16.0	75.2	20.1
1972	31.8	10.7	3.8	46.3	3.6	2.6	1.3	7.5	11.4	24.3	35.3	16.3
1973	34.6	10.7	4.0	49.3	3.9	2.3	1.8	8.0	11.4	21.9	44.3	16.3
1974[b]	40.4	14.3	4.8	59.5	3.4	2.9	2.4	8.7	8.4	20.3	50.0	14.6
1975	42.3	13.1	4.6	60.0	4.5	3.5	1.8	9.8	10.6	26.7	40.0	16.4
1976	42.8	14.3	4.8	61.9	5.7	4.5	2.2	12.4	13.3	31.5	45.8	20.0
1977	48.5	14.1	5.2	67.8	6.3	4.6	3.1	14.0	13.0	32.6	60.0	20.7

[a] First year that data was taken.

[b] In 1974 a more comprehensive data collection program was developed, resulting in a substantial increase over the previous year.

Coal ash may be categorized into three types: bottom ash, boiler slag, and fly ash. Bottom ash and boiler slag are removed from the bottom of a coal-fired boiler, while flyash exists with exhaust gases and must be removed by some type of particulate collection device. Current TVA practice is to grind bottom ash and slag, mix it with water, and convey it to an ash disposal pond. Similarly, fly ash is removed from the hoppers of mechanical cyclones, electrostatic precipitators, baghouses, and/or scrubbers and transported by a water stream to the ash disposal pond. Most of this ash remains in the disposal area.

Table 2 lists the ash production at the 12 TVA steam plants on a five year average basis. During calendar year 1978, approximately 0.7 million tons of coal ash were utilized rather than disposed of.[3]

TVA ASH UTILIZATION PROGRAMS

TVA's ash utilization program began in the 1950's with the use of flyash as a concrete admixture in the construction of the Wilson Dam Lock near Muscle Shoals, Alabama. Since that time, TVA has been actively involved in developing specifications for the use of flyash in construction projects.

The standard procedure in concrete procurement is for TVA to supply batching facilities and mix designs while the raw materials and equipment operations are provided by a private contractor. In this way, TVA is able to require the use of ash in its own construction and to promote the use of ash by private contractors. TVA experience has been that after using flyash as an admixture in a TVA construction project, most ready-mix concrete suppliers use ash in other projects.[1]

TVA promotion of ash utilization has included flyash as an admixture in concrete and boiler slag for roofing materials. Research has been conducted in other areas of ash use. Bottom ash is extensively used by the TVA power production staff in the maintenance of ash pond dikes and roads. During 1978, 281,250 tons of bottom ash were used for these purposes.[3]

FLY ASH UTILIZATION

Flyash used as an admixture in concrete must be collected and stored in the dry state. Four power plants in the TVA system (the Kingston, Colbert, Allen and Gallatin Steam Plants) are equipped to do this. Visits were made to each of these plants as a part of this study, and descriptions of the ash-handling operation at each plant are included as a part of the report.

Flyash is sold by TVA for both TVA and commercial construction uses. All deliveries are coordinated through the Division of Fossil and Hydro Power; Chattanooga, Tennessee.

Table 2. AVERAGE COAL USE AND ASH PRODUCTION BY TVA STEAM PLANTS 1971-1975.

Plant	Units	Coal Burned (Million Tons) per year	Bottom Ash (Thousand Tons)	Fly Ash Collected (Thousand Tons)	Fly Ash Released (Thousand Tons) to Atmosphere
Allen	3	1.4	115.3	47.4	3.8
Bull Run	1	2.3	68.4	245.4	35.9
Colbert	5	2.7	80.7	272.5	1.4
Cumberland	2	3.25	107.3	425.3	4.3
Gallatin	4	2.2	82.6	315.7	15.3
John Sevier	4	1.5	46.8	186.9	0.7
Johnsonville	10	2.9	82.5	333.3	94.2
Kingston	9	4.0	156.7	576.5	46.7
Paradise	3	6.1	867.3	282.8	6.3
Shawnee	10	4.6	141.4	557.6	8.9
Widows Creek	8	3.9	132.6	356.8	172.9
Watts Bar	4	0.3	23.5	20.7	1.2
Total	63	35.2	1898	3621	392

Source: Structural Section, Division of Fossil and Hydro Power, TVA

Kingston

Kingston steam plant is a 9 unit station rated at 1,700 MW(e). Fly ash collection at the Kingston Steam Plant is accomplished by mechanical collectors followed by two sets of electrostatic precipitators (the last set was installed in recent years in order to obtain greater particulate collection efficiency). The fly ash disposal system consists of a vacuum device which empties ash from the collector hoppers. The ash is then mixed with water and flows through a pipe to an ash disposal pond. The system serving the newest precipitators is independent of the previously installed one. A slip-stream of ash may be diverted from the older ash collection system to a 200 ton silo for storage. This silo is equipped to discharge ash into trucks. The dry handling system fills the silo at the rate of 10 to 15 tons per hour, according to operating personnel.

Table 3 lists the amount of ash sold by Kingston during 1978.

Colbert

Colbert Steam Plant consists of 5 units rated at a total of 1300 MW(e). The manner of removal of fly ash from the collector hoppers is similar to that of Kingston except that both the wet and dry handling systems may not be operated simultaneously and ash is conveyed only from units 3 and 4 by the dry system. Ash storage is in a 100 ton silo. Because of vacuum losses and other conveyance problems when fly ash is diverted into the storage silo, the hopper cleaning system is unable to keep the hoppers emptied. Therefore, ash may be collected for dry storage for only 4-6 hours before the wet disposal system must be employed.

Ash is sold only to commercial users from Colbert. The sales during the year 1978 are listed in Table 3.

Gallatin

Gallatin Steam Plant is a 4 unit station rated at 1,255 MW(e). The collection system and storage silo are similar to the installation at Kingston. A new 2,000 ton storage silo is under construction and should be completed during 1979. This silo is capable of serving both truck and rail carriers.

Table 3 indicates that the majority of ash utilized from Gallatin was delivered to TVA construction sites, primarily Hartsville Nuclear Plant, during 1978. Commercial sales from Gallatin are handled through a broker--Penn-Virginia Materials Company, Eastlake, Ohio. As TVA construction use declines, commercial markets for the Gallatin ash must be developed in order for its storage capacity to be fully utilized.

Allen

Allen Steam Plant consists of 3 units rated at 300 MW(e). The boilers are of the wet bottom type; i.e., the units are operated at temperatures above the ash fusion point. Molten slag is removed from the bottom of the furnace and is quenched in water, ground, then pumped with water to the ash

Table 3. TVA ASH PRODUCTION AND SALES - 1978

Plant	ASH PRODUCTION Bottom Ash (thousand Tons)	ASH PRODUCTION Fly Ash (Thousand Tons)	FLY ASH SALES TVA Construction (Thousand Tons)	FLY ASH SALES Commercial (Thousand Tons)	Boiler Slag Sales
Kingston	156.7	576.5	23.8	5.75	----
Colbert	80.7	272.5	---	3.15	----
Gallatin	82.6	315.7	31.9	19.77	----
Allen	115.3	47.4	---	---	194.5[a]

[a] Sales rates are greater than production rates because the slag ponds are being mined.

disposal pond.

The fly ash removal and storage system at Allen has been recently modified. A vacuum collector manifold empties the collector hopper. Operators have the option of sending all of the ash collected to two 200 ton silos or to a conventional wet disposal system. Allen is the only TVA plant able to remove and store all of the fly ash collected in a dry state.

Slag is removed from the Allen ash pond and sold for further processing. This is discussed below.

Dry Bottom Ash

As previously mentioned, the majority of the boilers in the TVA system are of the dry-bottom type producing bottom ash and slag. These materials are ground when collected and pumped to the ash disposal pond. Bottom ash and slag are usually discharged into a remote area of the pond where they may be later mined for use in ground maintenance.

TVA has sought to more extensively use bottom ash and slag as aggregate in asphalt pavement and as a base coarse material. During the period 1976-1978, TVA investigated the use of ash obtained from Kingston in asphalt paving mixtures. A demonstration project was constructed using power plant ash. The project course appears to be performing well. However, it was found during the course of the project that the ash was extremely variable, depending upon the portions of the pond from which it was obtained. High asphalt contents were required to produce an optimum mixture.

Wet Bottom Slag

As previously described, the term "wet bottom" applies to those boilers producing molten slag. The Allen and Paradise steam plants are of this design. Slag from these boilers has commercial value because of its consistent composition and uniform gradation.

The H.B. Reed Company is a manufacturer of blasting grit and roofing granules derived from boiler slag. As a part of the visit to the Allen Steam Plant, a tour was made of the Reed Company installation at Memphis, Tennessee.

H.B. Reed Company

The Reed plant at Memphis processes approximately 800 tons of raw slag per day. The manufacturing process is basically a size-fractionating operation. Material greater than 0.5 in. and less than a number 100 seive is not used but is sold to cement manufacturers as a raw material for Portland cement. After drying, the remaining material is fractionated into blasting grit (20%) and roofing granules (80%).

Fly ash is not suitable for this application because of its small particle size. Slag and bottom ash from the dry bottom boilers are also unsuitable since the small amount of carbon still present could combust during drying. Table 3 lists the sales of slag from Allen during 1978. Note that more slag was sold than was produced because previous years' productions of slag are being mined from the pond.

Reed Company has recently entered into an agreement with TVA to buy at least 150,000 tons per year of slag from the Paradise Steam Plant. The slag would be processed at the Memphis plant.[3] The agreement includes an option to build a processing plant at Paradise and to process up to 500,000 tons per year.

Cenospheres

Cenospheres, commonly referred to as "floaters," are hollow fly ash particles that float in ash ponds because of their low density (see Section 2 for cenosphere properties). Floaters have been collected for some time at TVA plants by skimmers to prevent them from exiting the pond with the effluent. Cenospheres are being removed from TVA ponds on a limited basis by Porter Warner Industries, Inc., this company is developing and evaluating various markets for cenospheres.

Section 2

PROPERTIES OF COAL ASH

PHYSICAL CHARACTERISTICS OF FLY ASH AND BOTTOM ASH

With respect to the utilization of coal ash, physical and chemical characteristics must be considered prior to using ash for any purpose--whether it be on-site disposal or for commercial purposes such as aggregate in concrete, asphalt, or soil. The ash is a result of unburned organic material and non-volatilized inorganic materials present after the combustion of coal in the furnace of a combustion unit. During the combustion phase, the ash is distributed into two parts: the bottom ash and the fly ash. The bottom ash is collected from the bottom of the furnace (a boiler unit) and may be dry bottom ash or wet bottom ash (commonly referred to as boiler slag--the molten state of the bottom ash).

The distribution of ash between the bottom and fly ash fractions is a function of the boiler type and coal type.[4] In cyclone furnace/boilers (wet bottom units), up to 85% of the ash may be collected as bottom ash (slag); while in the pulverized coal-fired boiler, up to 85% may be emitted as flyash.

(Ray and Parker[4] and Furr and Parkinson[5] have conducted thorough reviews of the physical ahd chemical characteristics of ashes in the United States. The reader is referred to these for in-depth information).

In general, the flyash makes up 15 to 85% of the ash and ranges in diameter from 0.5 to 100 microns. Typically, the mass-median diameter is in the range of 8-30 microns and is dependent upon the type of boiler and type of flyash collector utilized. The particles are generally spherical and solid in nature, with a light tan to gray appearance. The presence of significant alkaline materials results in a lighter color; those processes burning inefficiently result in excess carbonaceous material and a blacker appearance due to excess carbon. Also, the presence of excess alkaline materials or excess carbon generally produces ashes with a smaller fraction of spherical particles.

Fly ash may also contain very lightweight particles called cenospheres which consist of silicate glass spheres filled with N_2 and CO_2. These particles may comprise as much as 5% by weight, or 20% by volume of the flyash.[4] These spheres, although a problem for wet disposal due to their tendency to float, have a commercial value and will be discussed in Section 10 in more detail.

The actual physical characteristics of an ash cannot be predicted accurately but must be measured experimentally after a power plant is on-line. Discussions with commercial users of ash revealed that frequent analyses of both physical and chemical characteristics of ash were required to insure that the ash was acceptable for the intended use. Changing operating conditions can result in undesirable characteristics (such as increased carbon content) significantly different from the average characteristics of the ash.

Summary of Physical Characteristics of Coal Ash in the TVA System

Several studies which summarize the physical characteristics of coal ash produced in the Tennessee Valley Region have recently been conducted.[6,7] These studies included tests to determine one or more of the following characteristics:

1. Particle size and fineness
2. Specific gravity
3. Compaction
   a. Maximum dry density
   b. Optimum moisture content
4. Loss on ignition
5. Surface area (Blaine fineness)

Table 4 is a summary of typical data for fly ash taken at 10 TVA power plants. The variations in these properties are a function of the type of collector employed on each plant (cyclone-mechanical collector or electrostatic precipitator). Appendix A includes detailed data sheets typical of the analyses conducted on each coal fly ash.

A similar series of tests were conducted by Rose, et al., in 1979 for the 24 power plants located in Kentucky (several of which are in the TVA system).[7] In this study, the authors related the various parameters and identified the point of collection of the flyash and/or bottom ash. Figure 1, taken from that study, illustrates the relationship between the percent of fly ash passing the 325 mesh by the "wet wash" method used in hydraulic cement (ASTM C 430). The percent passing the 325 mesh generally ranges from 75-95+% for flyash collected by precipitators; for mechanical collectors the percent passing the 325 mesh is significantly less (40-75%) illustrating the coarser characteristic of this latter ash.

Blaine fineness, as measured by ASTM C 204, was also found to be affected by the type of collector and specifically related to the percent passing a No. 325 mesh sieve.[7] As shown in Figure 2, the Blaine fineness, a measure of the surface area per unit mass, varies significantly within a single particle collector category with ranges of 2500-6500 cm^2/gr for precipitator fly ash and 1500-2000 cm^2/gr for mechanical collector ash.

The specific gravity of the flyashes collected in the TVA system and in Kentucky ranged from 2.0-2.9.

Table 4. FLY ASH PROPERTIES BY TVA POWER PLANT

Plant	% -200	% -325	Blaine cm^2/gm	Surface Area cm^2/cm^3	Mean Dia. Microns	Specific Gravity	LOI (%)
Colbert	75.0	63.15 (56 - 91)	1940	4830	16.1	2.45	1.05 (1.56 - 13.6)
Shawnee	94.7	90.8	4173	10440	7.7	2.48	3.27
Gallatin	97.5	96.0 (77 - 99.3)	3920	8630	7.0	2.34	2.0 (1.7 - 4.2)
Kingston	93.6	92.0 (84.1 - 99.4)	3770	8715	7.05	2.31	3.0 (1.6 - 9.0)
Widows Creek	70.1	66.3	1750	3510	17.1	2.01	1.4
Paradise	91.8	90.1	2620	7290	8.2	2.78	2.65
Johnsonville	94.0	89.44 (94.8 - 99.6)	2810	7113	9.2	2.53	.88 (.5 - 8.5)
John Sevier	90.3	87.2 (95 - 99.8)	3675	8705	7.8	2.35	3.55 (1.9 - 4.2)
Cumberland	91.0	87.7	2620	6560	9.2	2.50	.30
Bull Run	83.9	81.4	2200	5105	11.9	2.30	3.60

( ) = 1971-1975 Range. Data on the point of collection (electrostatic or cyclone) is not available. Watts Bar and Allen plants were not analyzed.

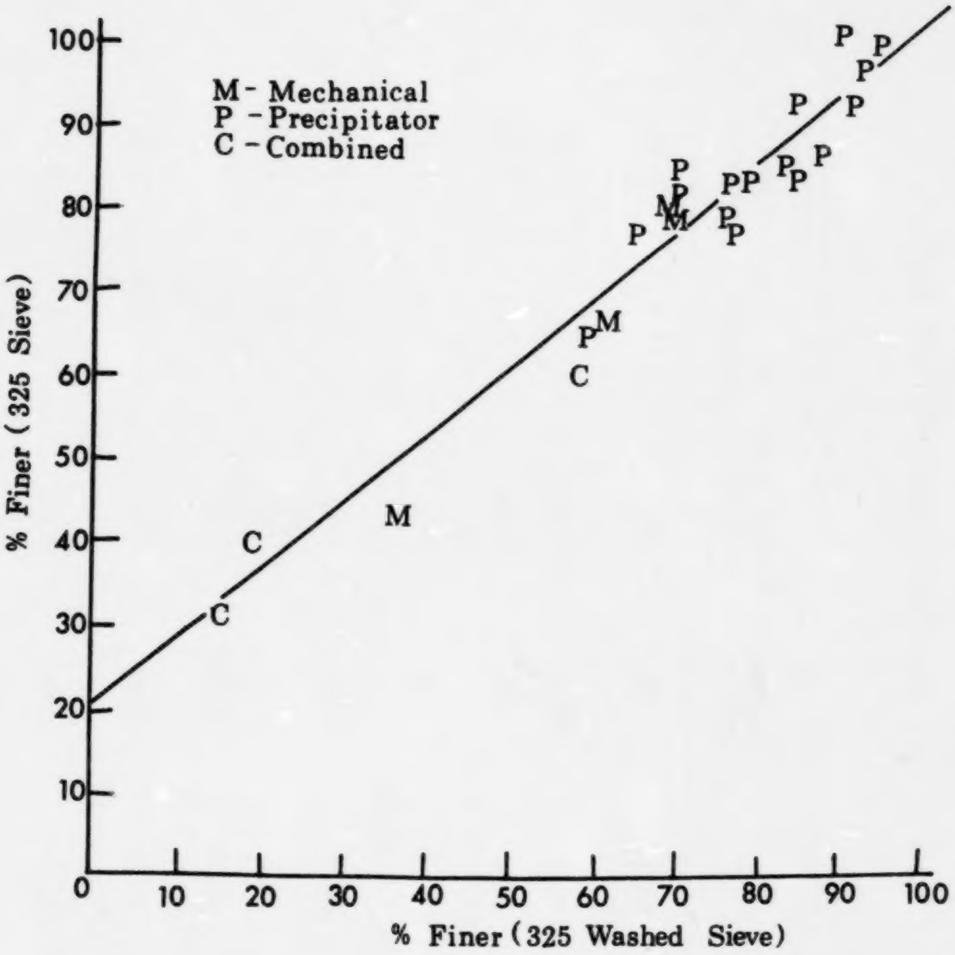


Figure 1. Fly Ash Fineness and Type of Collection Process

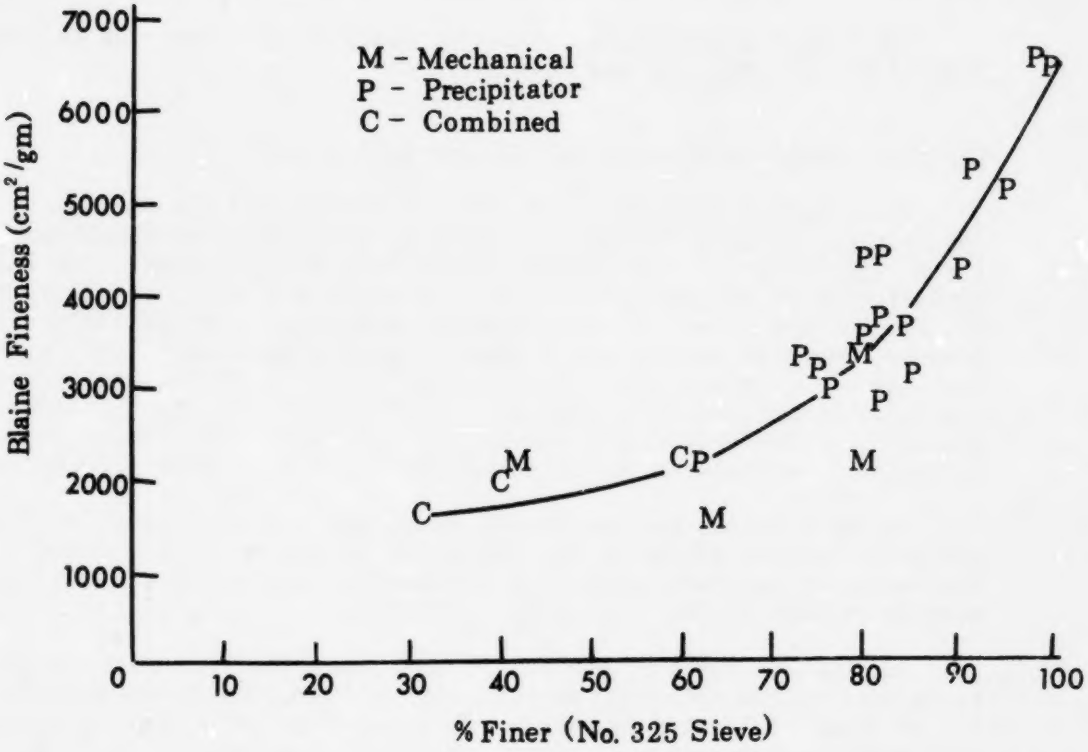


Figure 2. Blaine Fineness and Type of Collection Process

Compaction tests were also conducted on the Kentucky flyashes. Both maximum dry density and optimum moisture content (OMC) tests were performed (ASTM D 698, Method A). These data are shown in Figure 3[7] illustrating a range of values of dry density of 70-125 pounds/CF and OMC's of 10-35%. Typically the moisture content of the bulk flyash samples ranged from 0.03%.

The loss on ignition (LOI) of the flyashes for the Kentucky plants ranged from 0.95 to 9.34%[7], while the TVA system LOI's ranged from 0.3-3.27%. The boiler bottom ash/slag LOI's ranged from 0-33.14% for the Kentucky plants, showing a significantly larger variation than for the flyash. Also, the moisture content of the boiler slag ranged from 0.04 to 1.14%.

The size characteristics of boiler ash/slag were reported to range from 0.69-13.3% less than 200 mesh (74 microns).

CHEMICAL CHARACTERISTICS OF FLY ASH AND BOTTOM ASH

The chemical composition of ash is a function of the geological and geographical location of the coal deposit, the combustion conditions, and the air pollution control devices controlling the emissions. The inorganic constituents of ash are those typical of rocks and soils, primarily Si, Al, Fe, Ca, Na; the oxides of these elements comprise 95-99% of the ash.[4] Ash, however, may also contain small quantities of almost every other element. Furr, et al.[5], in a study of flyashes collected in 21 different states in the U.S., summarized the elemental content of each ash for 45 different elements. Their results are summarized in Table 5. The ranges in concentration are included in Table 5 as well as the pH range from 4.7 to 11.8.

In the previous section it was shown that the particle size of the ash was significantly different for the boiler bottom ash/slag and the fly ash. Similarly, it has been found that the chemical content of the ash is frequently related to the size of the particles.

As shown in Table 6, Ray and Parker[4] summarized the tendency of elements to be distributed by size. Further studies conducted on the chemical analysis of flyash collected by mechanical versus high efficiency collectors have also shown partitioning of elements by size. Kaakinen, et al.[8], found that Mo, As, Zn, Sb, Pb, and Cn significantly increased in concentration (referred to as enrichment) as the flyash proceeded through the boiler and control devices. In general, the degree of enrichment increased as the flyash progressed downstream from bottom ash to mechanical collector ash to electrostatic precipitator ash to ash emitted from the stack. The concentrations at the precipitator outlet were approximately 15 times those found in the bottom ash. The observed enrichment was attributed to the fact that the particle size decreased as the flyash progressed downstream due to preferential removal of the larger particles in the control devices. Specific chemicals tend to accumulate on smaller particles due to absorption, adsorption, and condensation phemonena due to the increased surface area per unit volume of the smaller particles.

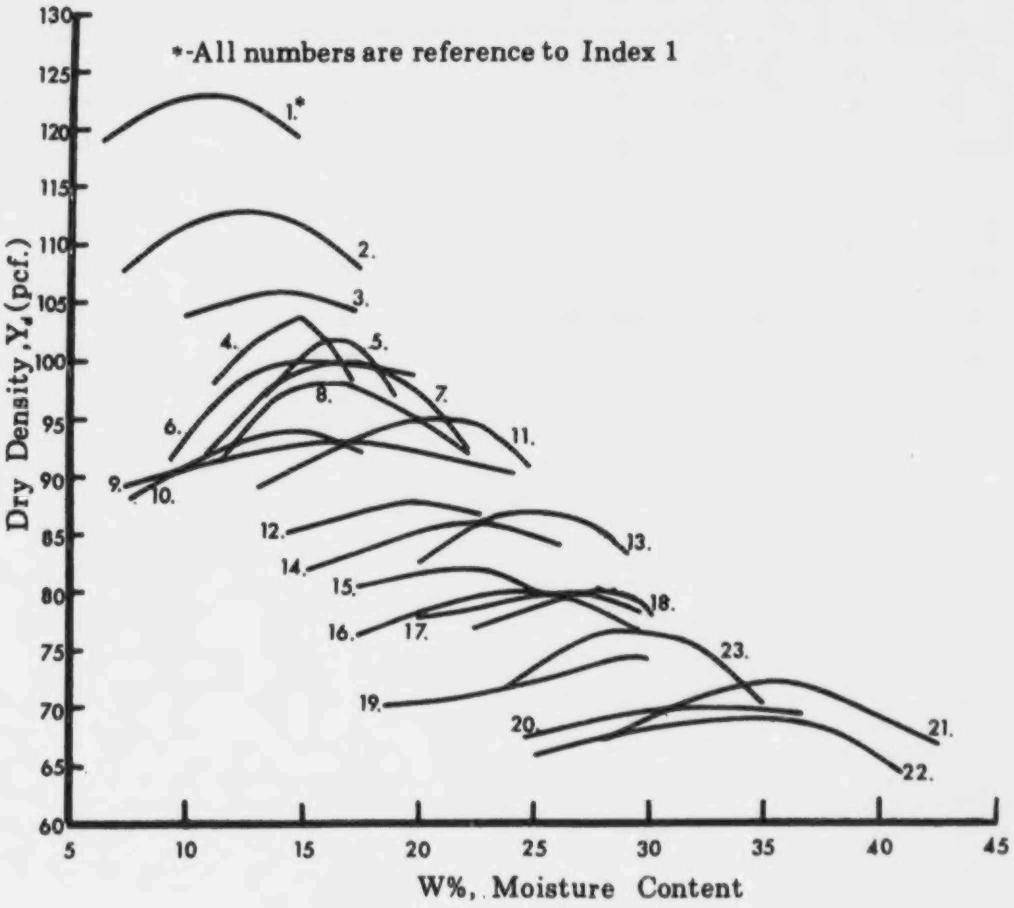


Figure 3. Dry Density vs. Moisture Content for the Fly Ash Samples

Table 5. RANGE OF VALUES OF ELEMENTS IN 21 FLY ASHES[5]

Element	ppm (dry weight basis)	Element	ppm (dry weight basis)
Al	59,100 - 135,100	Lu	.5 - 1.5
As	11 - 312	Mg	11,500 - 60,800
Au	.004 - .08	Mn	58 - 460
B	10 - 600	Mo	6.5 - 41
Ba	618 - 6,917	Na	1,180 - 18,400
Br	.3 - 21	Ni	1.8 - 115
Ca	7,250 - 163,300	Pb	3.1 - 241
Cd	.1 - 3.9	Rb	36 - 300
Ce	74 - 300	Sb	2.6 - 13.0
Cl	13 - 460	Sc	6 - 28
Co	4.9 - 73	Se	1.8 - 17
Cr	43 - 259	Sm	5.4 - 24
Cs	7.7 - 18	Sn	27 - 334
Cu	45 - 616	Sr	59 - 3,855
F	.9 - 46	Ta	.5 - 2.6
Fe	27,130 - 289,900	Th	22 - 68
Ga	13 - 230	Ti	2,758 - 8,310
Hg	.02 - .7	U	.8 - 19.0
I	.6 - 20	V	68 - 442
In	.1 - 1.1	W	2.9 - 21
K	1,534 - 34,700	Yb	1.7 - 7.0
La	33 - 104	Zn	14 - 406

Table 6. PARTITION OF ELEMENTS BY THEIR TENDENCIES FOR DISTRIBUTION IN COAL COMBUSTION RESIDUES[4]

Group I

Elements Comparably Concentrated in Bottom Ash and Flyash

Al	Ce	Fe	La	Rb	Sm	Th
Ba	Co	Hf	Mg	Sc	Sr	Ti
Ca	Eu	K	Mn	Si	Ta	

Group II

Elements Preferentially concentrated in the Flyash

As	Ga	Sb
Cd	Mo	S†
Cu	Pb	Zn

Group III

Elements Tending to be Discharged to Atmosphere as Vapors

Hg	Cl^-
S†	Br^-

† Majority of S is discharged as vapor; however, a significant portion of fly ash content also contains S.

Studies have also been conducted to measure the radiochemical characteristics of coal and coal ash. Specifically, measurements have been made of the concentrations of radium, thorium, and uranium.[83,84] Radiochemical analyses reported by Krieger and Jacobs[84] showed that radioactive emissions from both flyash and bottom ash were significantly greater than for the coal. The gamma ray activity for Louisville, Kentucky, power plant flyash was found to be as follows (where the activity is listed in parenthesis beside each element): ^{226}Ra (3.8-7.0 pCi/g); ^{234}U (4.2-6.3 pCi/g); ^{235}U (.2-.3 pCi/g); ^{238}U (4.4-8.6 pCi/g); ^{228}Th (1.8-1.9 pCi/g); ^{230}Th (4.5-6.5 pCi/g); and ^{232}Th (1.6-1.8 pCi/g). The range of values represented radiochemical analyses obtained on two different dates approximately one year apart. Analyses of the bottom ash showed radioactivity levels ranging from 0-36% less than the flyash, dependent on the element.

Section 3

ASH DISPOSAL

There are three types of coal burning furnaces: stoker, cyclone, and pulverized coal. Stoker furnaces are generally not used for large utility systems, and no stoker furnaces are in operation in the TVA power network.

In both the cyclone and pulverized coal furnaces, exhaust gases carry fly ash which is removed from the exit gas stream via the air pollution control system. Due to higher operating temperatures and ash fusion in the furnace, cyclone furnaces generate less fly ash than do pulverized coal furnaces.[34] Inversely, cyclone furnaces generate larger amounts of bottom ash and slag.

Fly ash removal in the air pollution control system is either wet or dry. Wet systems include wet scrubbers which are designed to remove fly ash simply or in conjunction with sulfur dioxide. Dry systems include dry air pollution control systems (cyclones, bag filters, electrostatic precipitators) which either remove fly ash by themselves or in combination with dry additive (lime, sodium, ammonia) sulfur dioxide removal systems. Wet systems obviously generate wet ash for disposal. Dry collection systems can generate either a wet (sluiced) or dry ash for disposal.[34] Dry ash disposal systems generally involve either some reuse or recycle, or the dry ash is wetted down to control dust and taken to a designed landfill area.[34]

Bottom ash is characterized as to the type of boiler used. Pulverized coal furnaces are either wet bottom type (molten ash) or dry bottom (solid ash) type. Cyclones create a molten ash on the walls of the cyclone. This molten ash runs out of the burner onto the furnace floor. In the wet bottom boiler, the molten ash is quenched in water, crushed, and then sluiced to the disposal area. In the dry bottom boiler, ash is crushed, and sluiced to the disposal area. Therefore, in both cases, a "wet" ash results.[34] Generally, this "wet" ash is ponded either separately or in the same pond with the fly ash or scrubber sludge. When the pond volume is exhausted, either the ponds are excavated for subsequent disposal or covered over.[35]

Table 7 presents a summary of the ash generation and disposal characteristics of plants in the TVA region. The discussion in Section 1 on the TVA ash utilization program presents details on specific ash disposal systems.

Table 7. TVA ASH GENERATION ADN DISPOSAL CHARACTERISTICS

Plant	Boiler Type	Bottom Type Generation	Fly Ash Collection	Bottom Ash Conveyance	Ash Disposal Bottom Ash	Ash Disposal Fly Ash
Allen	Cyclone	Wet Bottom	Dry	Wet	Wet	Dry
Bull Run	Pulverized Coal	Dry Bottom	Wet	Wet	Wet	Wet
Colbert	Pulverized Coal	Dry Bottom	Dry & Wet	Wet	Wet	Dry & Wet
Cumberland	Pulverized Coal	Dry Bottom	Wet	Wet	Wet	Wet
Gallatin	Pulverized Coal	Dry Bottom	Dry & Wet	Dry & Wet	Wet	Dry & Wet
John Sevier	Pulverized Coal	Dry Bottom	Wet	Wet	Wet	Wet
Johnsonville	Pulverized Coal	Dry Bottom	Wet	Wet	Wet	Wet
Kingston	Pulverized Coal	Dry Bottom	Dry & Wet	Wet	Wet	Dry & Wet
Paradise	Cyclone	Wet Bottom	Wet	Wet	Wet	Wet
Shawnee	Pulverized Coal	Dry Bottom	Wet	Wet	Wet	Wet
Widows Creek	Pulverized Coal	Dry Bottom	Wet	Wet	Wet	Wet
Watts Bar	Pulverized Coal	Dry Bottom	Wet	Wet	Wet	Wet

Section 4

FLY ASH UTILIZATION IN CONCRETE MIXTURES

INTRODUCTION

The use of fly ash in ready-mix concrete is considered to be one of the most promising areas for ash utilization. This is due to the fact that fly ash can be used to partially replace cement, which is the highest cost ingredient of concrete. Because the market for ready-mix concrete is stable and growing, long term utilization of fly ash can be assured as long as there is an economic savings in using fly ash as a fine aggregate as well as cement substitute. At this time, with the increasing cost of energy, the cost of cement production will undoubtedly increase since energy is a principal ingredient of cement production. It should be recognized that because of the varying properties of fly ash, and because the source of fly ash must be economically transportable to the concrete batching operation, the economics of fly ash utilization in concrete is site specific. In some places, fly ash is currently being transported up to 500 miles for utilization. Thus, in many cases fly ash utilization in concrete will represent a cost savings as well as a potential for increased concrete production.

The ingredients used in producing conventional Portland Cement concrete are Portland Cement, water, gravel, sand, and a variety of chemicals called admixtures.[55] The amounts of each of these ingredients affect the properties of the resulting concrete. Admixtures are materials that are added to concrete at some stage in its production. They give the concrete new properties either when in a fluid and/or in the set or cured condition.[55] Admixtures differ from additives in that additives are materials which are added during its manufacture as an aid to production or to give the concrete some special property.

Admixtures are generally classified into eight categories:[56] (1) Accelerating, (2) Retarding, (3) Water-Reducing/Plasticising, (4) Air Entraining, (5) Waterproofing, (6) Pumping, (7) Superplasticisers, and (8) Miscellaneous. In the miscellaneous category, one subcategory is called "finely divided materials." Among the finely divided materials, one can consider two types: inert and pozzolanic. Of special interest here are finely divided pozzolans (i.e., pozzolanic material).

Pozzolans are materials which by themselves have no strength-producing properties or cementing properties. Basically, they are siliceous and aluminous materials that, when finely divided, will react chemically with calcium hydroxide (lime) in the presence of water to form an adequate cementing material.[53]

Pozzolans can be either natural or artificial, such as pulverized fuel or fly ash. Pozzolans are added for increased strength, improved workability of the concrete mix, and reduced bleeding and segregation. (Bleeding occurs when the mix water tends to rise to the surface of fresh concrete as solids constituents settle downward.[54] Bleeding tends to lead toward weak concrete subject to disintegration.) Other advantages associated with pozzolans are greater resistance to freezing and thawing and resistance to attack by sulphates. In addition, pozzolans can be used to replace a proportion of the cement, thereby leading to lower concrete costs whenever the additional pozzolan costs are offset by the saving associated with lower cement content.

The main justification for using pozzolans is the possibility of reducing costs. Unless a worthwhile reduction in cost can be made by a savings in the amount of cement used, it is doubtful whether a case can be made for general use.[50] However, economic incentives by utilities to concrete batchers may make the use of a pozzolan-like fly ash economically justifiable in concrete, at a cost that is less than that of ultimate disposal by the utility even when the savings in concrete reduction do not justify its use.

Fly ash normally contains a silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), carbon in the form of unburnt fuel, calcium oxide (CaO), and small quantities of magnesium oxide (MgO) and sulfur trioxide (SO_3). When using fly ash as an admixture in concrete to serve as a pozzolanic material, several properties are important. First, the material should be finely divided. Fly ash obtained from electrostatic precipitators is generally finer than Portland Cement; therefore, it is very suitable without considerable processing. Second, the carbon content of the ash plays an important role in the amount of entrained air.[53] Generally, the amount of entrained air is depressed with the use of fly ash. Since the amount of entrained air is important for strength and other properties, the control of entrained air in fly ash concrete is important.

Concrete containing small air bubbles (.05 mm/1.25 mm) spaced at gaps less than or equal to .4 mm evenly distributed throughout its bulk is more durable to freeze/thaw action than normal concrete.[55] Air entrained concrete in the plastic state is more workable. It can usually be placed with less segregation and bleeding. However, air entrainment does result in some strength loss. All air-entraining agents are surface active and reduce the surface tension at the water/air interface. This means that minute bubbles that form remain as stable bubbles and do not collapse.

Controlling the right amount of an air-entraining agent is very important. Since the carbon residue in fly ash has the ability to absorb most air entraining admixtures, usually more air entraining agent needs to be added when fly ash is included in the concrete. It has been stated that concrete made with a fly ash that has a four percent carbon content needs twice the amount of air entraining agent than needed conventionally.[53] This plays a role in the economics of fly ash utilization in concrete.

VARIATIONS IN STRENGTH DUE TO FLY ASH

Concrete can be classified as either non air entrained (natural air content .3 to 3 percent by volume) or air entrained (air content ranges from 3.5 to 8 percent).[50] As mentioned previously, air entrained concrete tends to have a higher resistance to freezing and thawing damage. Most industrial and commercial structures today are built with air entrained concrete. Unfortunately some loss of compressive strength occurs with increasing air volume above that level naturally occurring in a mixture.[53]

Figure 4 depicts the relationship between the compressive strength and the curing age of the concrete when Type I Portland Cement is used. In order for the concrete to develop to its full strength, it is necessary for moisture to remain in contact with the cement. If this is not the case, full strength is not realized. The early strength of the concrete is important in that it determines the time necessary before loads can be placed on the concrete. Bloem has shown that curing conditions affect fly ash concrete in a manner similar to that of plain Portland Cement concrete.[60]

The general trend is that replacement of up to 30 percent of the cement by fly ash tends to lower the compressive strength during the period of 7 to 28 days and raise the compressive strength at ages beyond 90 days as compared to normal portland cement concrete.[53] This is due to the fact that pozzolanic action is slow to develop. Elevated temperatures speed up the pozzolanic action, so fly ash concrete placed in warm weather will have higher earlier strengths as compared to that placed in colder weather. However, the general approach used to assure early strength that is comparable to Portland Cement concrete for a fly ash concrete is to have a slightly higher 28 or 90 day design strength. In many cases the lower strength during the 7 to 28 day period should not be of great concern, since it is usually within 85% of the strength of the comparable Portland Cement concrete.

ECONOMICS OF FLY ASH CONCRETE

In order to estimate the cost of fly ash concrete, a number of factors need to be assumed. First, the cost of fly ash at a batching facility is a function of the cost of the fly ash as well as the cost of the transportation and handling. Second, fly ash utilization in concrete requires special equipment for storage and handling at the batching plant. Third, the savings in cement in making fly ash concrete is a function of the type of concrete and desired properties. In order to make some estimates, let's assume that the fly ash is available at $4/ton and that the batching facility is 50 miles from the power plant. If it costs $6/ton to handle and transport, then the fly ash at the batching site would be $10/ton. If the extra handling equipment costs an additional $5,000 per year, if there is an additional maintenance of $2,000 per year at the batching plant, and if we assume a use of 2000 tons per year of fly ash, then the cost per ton at the batching plant (including handling) is $10 plus $3.50, which equals $13.50 per ton.

Currently, cement costs $47/ton plus transportation. To estimate the savings, if any, the type and strength of the concrete must be specified.

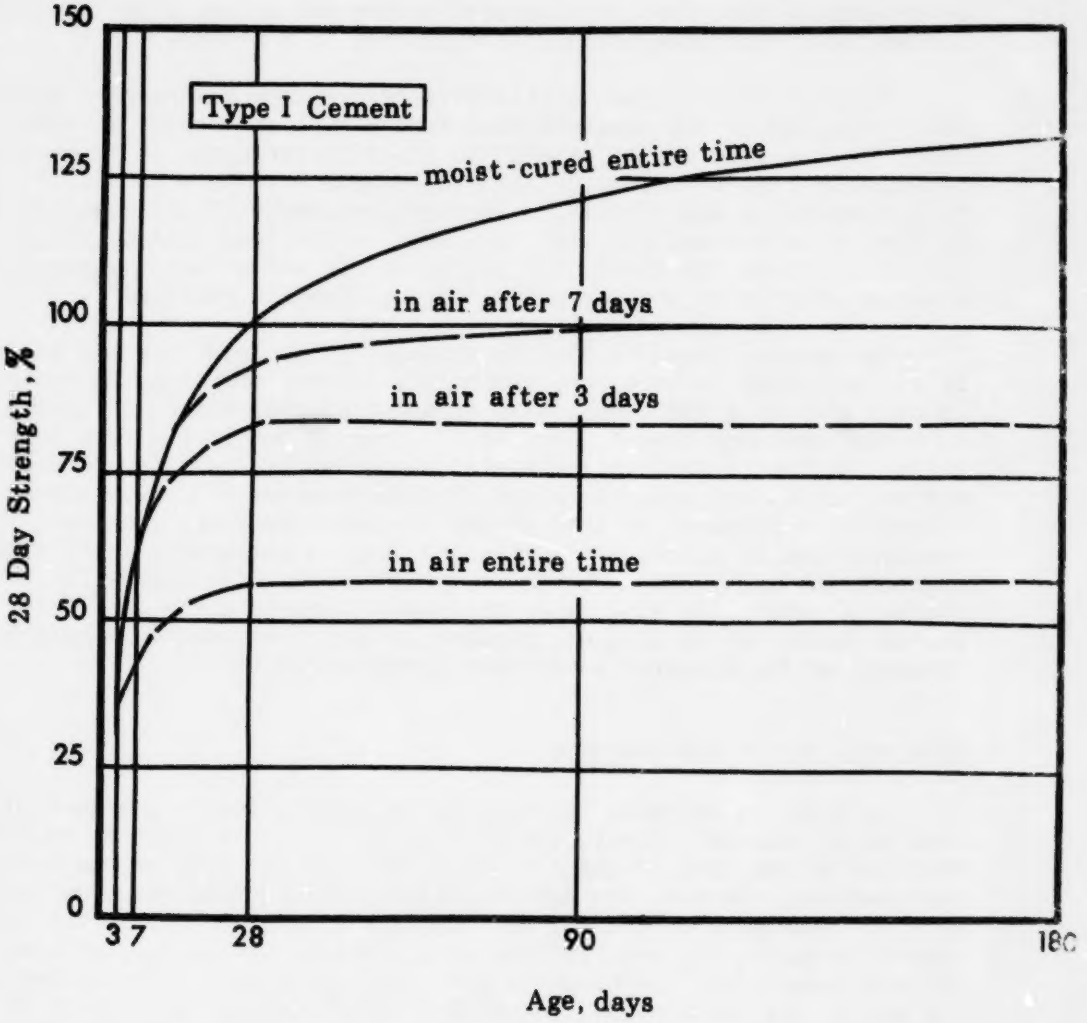


Figure 4. Curing Conditions and Strength of Portland Cement Concrete

If a 3000 psi air entrained concrete was specified, then one could use the following amounts for one cubic yard:

	Air Entrained Concrete	Air Entrained Fly Ash Concrete
Cement	470 lb.	400 lb.
Fly ash	---	125 lb.
Air entraining agent	5 lb.	10 lb.
Aggregates	3200 lb.	≅3200 lb.

For the cost side, we can estimate:

	Air Entrained Concrete	Air Entrained Fly Ash Concrete
Cement	$11.05	$ 9.40
Fly ash	---	.85
Air entraining agent	.05	.10
Aggregates	3.20	3.20
	$14.30	$13.55

From this calculation we can see that a difference of 75 cents per yard exists. Thus, a savings of greater than 5 percent can be achieved by utilizing fly ash in this case. Obviously, costs are a function of the cost of fly ash, and any savings would be based on the cost of fly ash.

It should be realized that the costs can change considerably based on the total transportation costs of both fly ash and cement. The transportation cost of cement was not considered in the above example, and would more than likely add an additional differential of 25 cents per cubic yard. It is safe to state that future differentials are likely to be larger and in favor of fly ash utilization because the cost of cement manufacture is a function in large part to energy costs. In the early 1970's energy cost accounted for only 10 percent of total cement manufacturing costs. However, energy costs are now close to 30 percent of total costs and are likely to be even higher with new source performance standards on cement plant emissions.

Section 5

FLY ASH AND MINERAL RECOVERY

BACKGROUND

It has been recognized that coal ashes contain large concentrations of aluminum and iron as well as lower concentrations of Ti, U, Th, Cr, V, Ni, Co, and Zn. Concepts for recovering these materials existed 50 years ago but were not economic.[36]

Three facts today may make recovery more feasible. First, the cost of mining, extraction, and transportation of primary metals is rising rapidly. Second, many metals used in United States industry are imported in high percentages and the concern over international cartel control of these minerals is increasing.[37] Third, the recovery of metals may reduce the volume of residual solids that require disposal.

RECOVERY TECHNIQUES

Presently seven techniques have been proposed for recovery of metals. Each technique will be discussed. Comparison of the techniques will not be made as only two (lime sinter and lime soda sinter) have been demonstrated on an engineering scale. Finally, a discussion will be presented related to product recovery techniques:

1. Lime Sinter: Fly ash is first sintered at 1200-1300°C with powdered limestone where the silica is fixated and soluble aluminate compounds are formed. The aluminates are then dissolved from pulverized sinter in an aqueous soda ash solution, which is then precipitated as aluminum trihydrate which is separated and calcined to alumina.[38] Magnetic separation of iron prior to fly ash processing is recommended as a means of increasing aluminum yield.[38]

2. Lime-Soda Sinter: When soda ash is also in the sinter with limestone, sodium aluminate is formed along with calcium silicate and calcium aluminate. In the sinter reaction the lime combines with silica to form dicalcium silicate:

$$2\ CaCO_3 + SiO_2 \rightarrow 2\ CaO \cdot SiO_2 + 2\ CO_2 \qquad (1)$$

This reaction frees the aluminum which was combined with the silica. This alumina reacts with soda ash or limestone to form soluble aluminates:

$$12\ CaCO_3 + 7\ Al_2O_3 \rightarrow 12\ CaO \cdot 7\ Al_2O_3 + 12\ CO_2 \qquad (2)$$

$$NaCO_3 + Al_2O_3 \rightarrow Na_2O \cdot Al_2O_3 + CO_2 \qquad (3)$$

The aluminates are then dissolved via a soda ash solution, and treated with lime to precipitate silica. The tailings from the leaching step are sintered and mixed with gypsum during grinding to form Portland Cement.[39]

Magnetic separation of the fly ash is again advisable to increase aluminum yield.[38] The $CaO:SiO_2$ mole ratio should be 2 with excess CaO to give a $CaO:Al_2O_3$ mole ratio of 12:7 or enough Na_2CO_3 to give a $Na_2O:Al_2O_3$ mole ratio of 1:1.[38] Figure 5 presents a flow diagram of the lime-soda-sinter process.[39] Studies at the Department of Energy's Oak Ridge National Laboratory (ORNL) indicated aluminum recoveries were in the 60-70% range.[39]

3. Direct Acid Leach: Samples of fly ash were leached, at ambient temperatures, with HCl, HNO_3, and H_2SO_4. Low recoveries were observed to be: 15% Al, 60% fe, 35% U, and 17% Ti.[39]

The same ashes were treated with the same acids under reflux conditions for six hours and recoveries were observed to be: 56% Al, 73% Fe, 40% Ti, 74% U.[39] Low recoveries on fly ash can be expected since the ash consists of iron and aluminum silicates along with silica which is fused into refractory glassy material.

4. Salt-Soda Sinter: ORNL developed a modified sintering process (Figure 6) to recover aluminum and other metals from fly ash.[38,39] A fusion mixture of $NaCl\text{-}Na_2CO_3$ (weight ratio of 2:1) is mixed with fly ash on a weight ratio of 3:1, heated to 800°C to sinter, quenched in water, and leached in diluted HNO_3 or H_2SO_4. Fe, Ti, and U are solubilized and aluminum recovery exceeds 95%.[38,39]

5. Calsinter: ORNL also studied a sinter process (Figure 7) where fly ash was sintered at 1000-1300°C with a mixture of gypsum and limestone. The sinter is followed by leaching with H_2SO_4. Using 1:1:1 weight ratio of fly ash, gypsum, and limestone and $4NH_2SO_4$, the following recoveries were observed[38,39]: Al-97%, Fe-90-95%, Ti-90-95%, U-80%, Mn-70%.

Studies have been conducted to substitute FGD scrubber sludge for gypsum and some of the limestone in the Calsinter process. As the sintering temperature increased to 1200°C and the ratio of sludge solids to fly ash ratio increased, Al recovery improved to more than 95%.[39] Figure 7 presents options for product recovery which include either extraction or continuous ion exchange.

6. Hi-Chlor: DOE's Ames Laboratory has developed a process utilizing the non-magnetic fraction of fly ash where upon carbon is added as a reductant to react with oxygen released from oxides and is then chlorinated at 800-900°C[40]:

$$\underline{SiO_2} + \underline{2C} + 2\ Cl_2(g) \rightarrow SiCl_4(g) + 2\ CO\ (g)$$

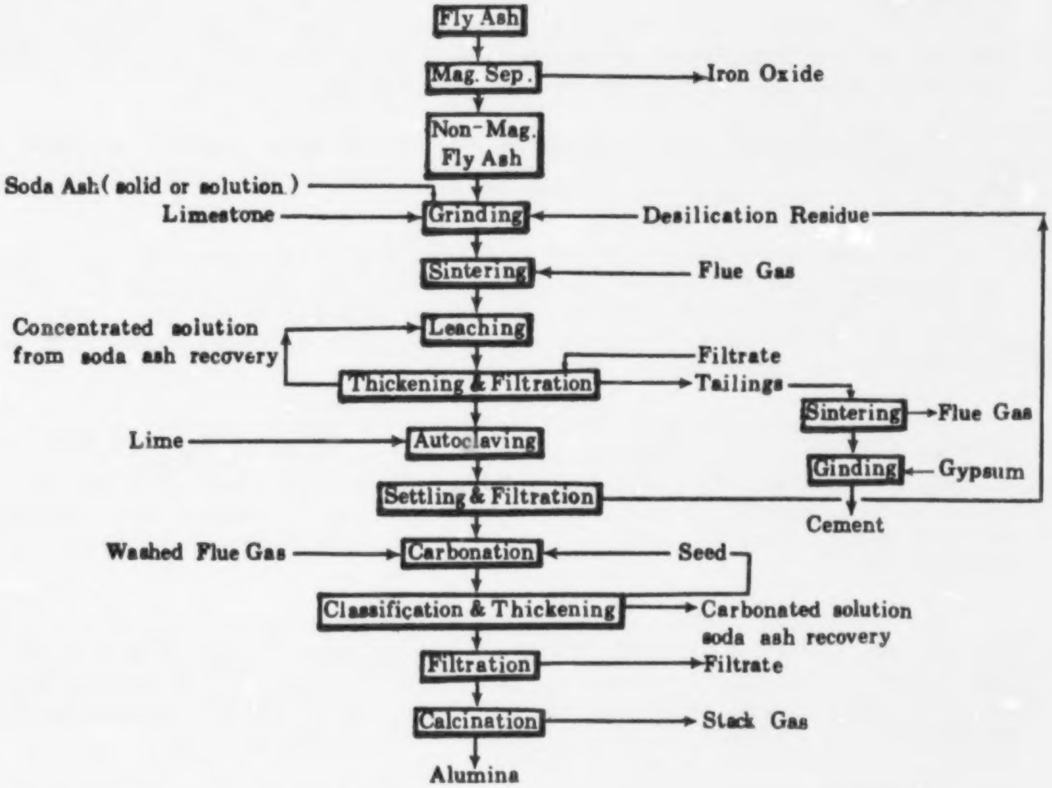
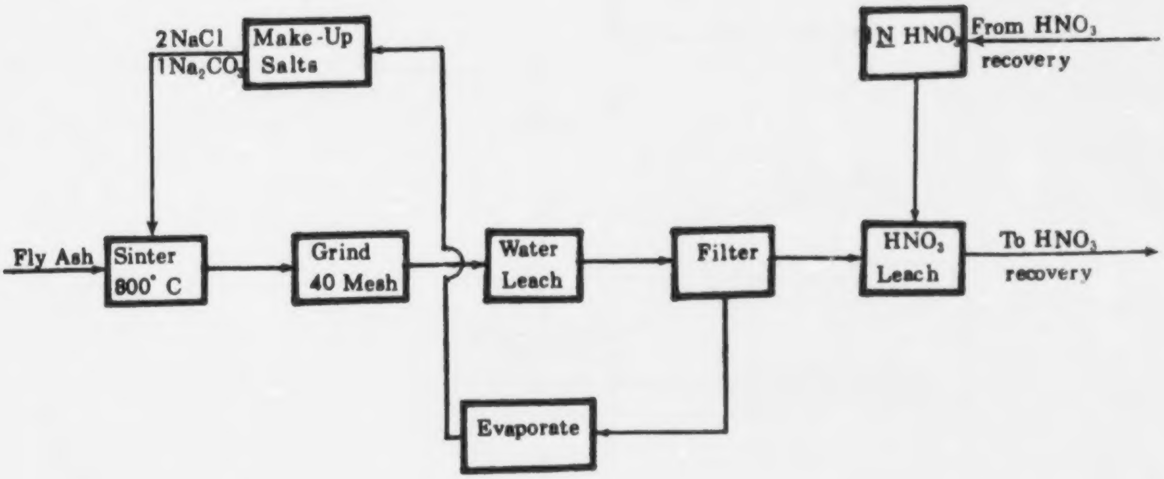

Fly Ash
Mag. Sep.
Iron Oxide
Non-Mag. Fly Ash
Soda Ash(solid or solution)
Limestone
Grinding
Desilication Residue
Sintering
Flue Gas
Concentrated solution from soda ash recovery
Leaching
Filtrate
Thickening & Filtration
Tailings
Sintering
Flue Gas
Lime
Autoclaving
Ginding
Gypsum
Settling & Filtration
Cement
Washed Flue Gas
Carbonation
Seed
Classification & Thickening
Carbonated solution soda ash recovery
Filtration
Filtrate
Calcination
Stack Gas
Alumina

Figure 5. Generalized Flowsheet for the Lime-Soda Sinter Process[36,39]



2NaCl
1Na₂CO₃
Make-Up Salts
1N HNO₃
From HNO₃ recovery
Fly Ash
Sinter 800° C
Grind 40 Mesh
Water Leach
Filter
HNO₃ Leach
To HNO₃ recovery
Evaporate

Figure 6. Generalized Flowsheet for the Salt-Soda Sinter Process[36,39]

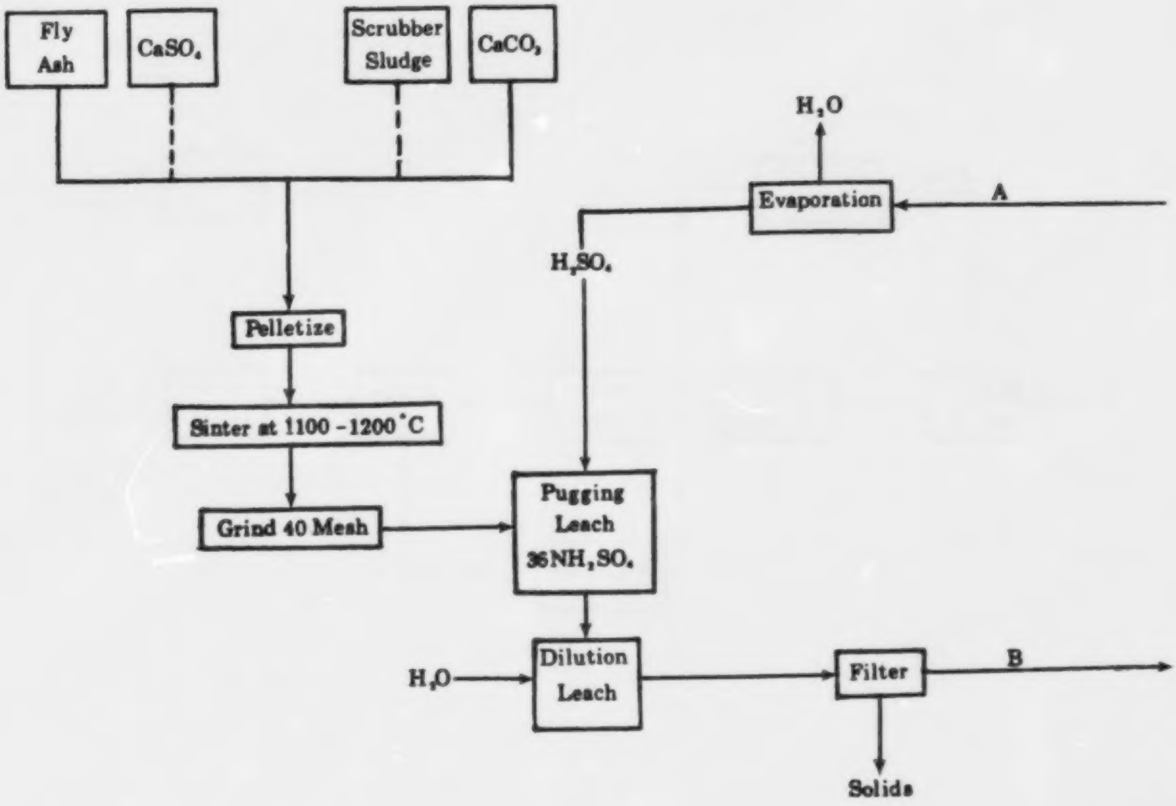

Fly Ash
CaSO4
Scrubber Sludge
CaCO3
H2O
Evaporation
A
H2SO4
Pelletize
Sinter at 1100 - 1200°C
Grind 40 Mesh
Pugging Leach 36NH4SO4
H2O
Dilution Leach
Filter
B
Solids

Figure 7. Generalized Flowsheet for the Calsinter Process (36,39)

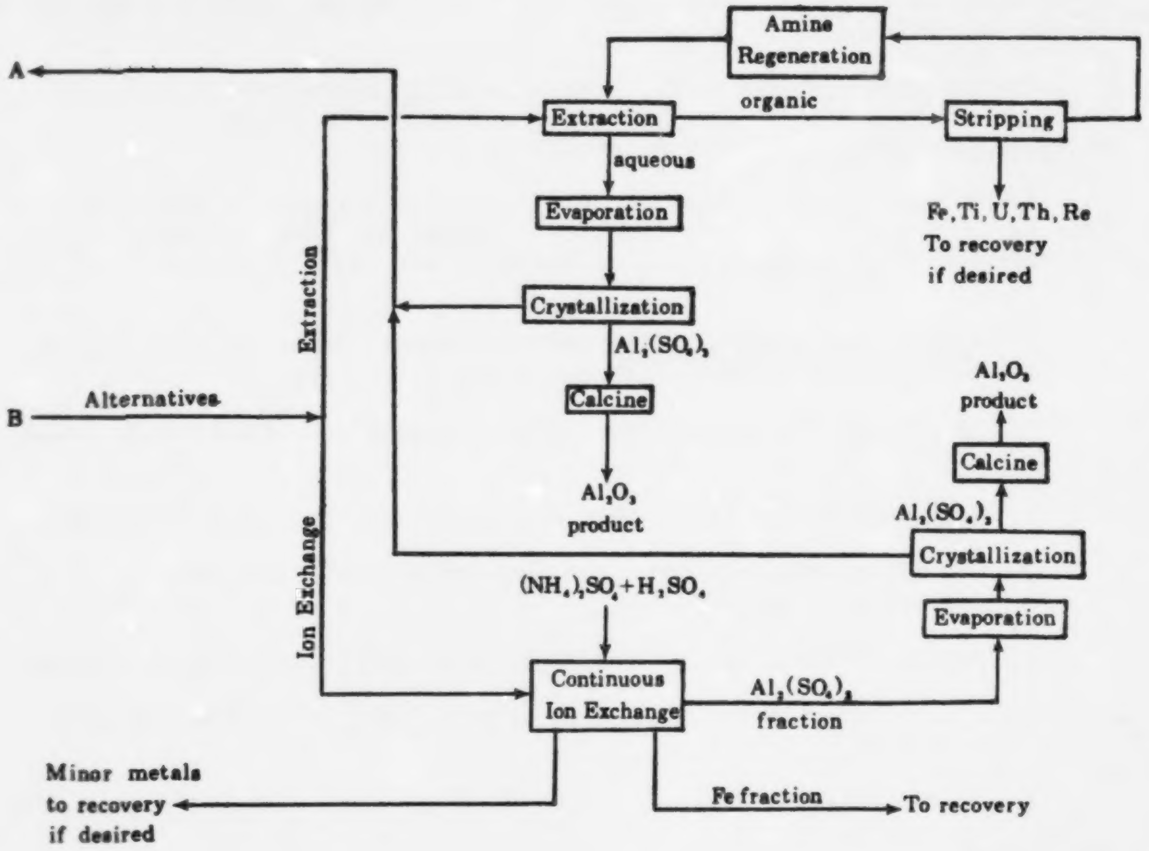

Amine Regeneration
A
Extraction
organic
Stripping
aqueous
Evaporation
Fe, Ti, U, Th, Re
To recovery if desired
Extraction
Crystallization
$Al_2(SO_4)_3$
Calcine
B
Alternatives
Al_2O_3 product
Al_2O_3 product
Calcine
$Al_2(SO_4)_3$
Crystallization
Ion Exchange
$(NH_4)_2SO_4 + H_2SO_4$
Evaporation
Continuous Ion Exchange
$Al_2(SO_4)_3$ fraction
Minor metals to recovery if desired
Fe fraction
To recovery

Figure 7. (Continued)

$$\underline{Al_2O_3} + \underline{2C} + 3\ Cl_2(g) \rightarrow 2AlCl_3(g) + 3\ CO\ (g)$$

$$\underline{Fe_2O_3} + \underline{3C} + 3\ \underline{Cl}_2(g) \rightarrow 2FeCl_3(g) + 3\ CO\ (g)$$

$$\underline{TiO_2} + \underline{2C} + 2\ Cl_2(g) \rightarrow TiCl_4(g) + 2\ CO\ (g)$$

Although difficult, this process is proposed to remove the metal chlorides from the off-gas by absorption into fused salts followed by serial phased distillation for recovery of relatively pure $FeCl_3$, $AlCl_3$, $TiCl_4$, and $SiCl_4$. $SiCl_4$ would be recycled to the reactor to control formation of this probably undesirable product.[40]

The principal product, $AlCl_3$, can be used for production of Al metal. $TiCl_4$ can be converted to TiO_2 which has a market value of \$900/ton[40] Recoveries have been 70-80% for Al, 80-90% for Fe, and 70-80% for Ti.[40]

Since some iron will remain in the non-magnetic fraction, and since iron has a strong affinity for Cl_2, it is recommended that the remaining iron be removed as volatile $FeCl_3$ at 400-600°C whereas Al, Si, and Ti do not react until 800°C.[40]

7. Mineral Gas Company (MGC): MGC of Memphis, Tennessee[41] has a patent on a mineral recovery process which can be applied to fly ash.

The process at its present level of development consists of five primary steps:

1. Precondition the ash at 90°C with a solution of sodium hydroxide.
2. Solubilize the aluminum, iron, and other metals in a bath of hydrochloric acid.
3. Remove 60-65 percent of the iron via an electrical plating process.
4. Precipitate the remaining iron with the recycled sodium hydroxide from step 1.
5. Precipitate the aluminum oxide with a solution of hydrochloric acid.

All reagents used are recycled and the process uses a relatively low heat input when compared with other recovery processes. Laboratory test results indicate that iron, iron oxide, and aluminum oxide can be removed economically.

MGC has also developed a second process to extract aluminum sulphate (alum) directly from fly ash.

8. End Product Options: ORNL[39] has summarized end product options as follows:

1. Recovery of the aluminum as ammonium alum from Calsinter leach solutions by neutralization of the acid with ammonium hydroxide.

2. Crystallization of aluminum chloride by evaporation of the leach solution to approximately 72% sulfuric acid followed by saturation of the liquid with anhydrous HCl.

3. Extraction of the iron, titanium, manganese, and uranium into an organic compound containing 30% primary amine in a suitable diluent, and crystallizing the aluminum sulfate left in the raffinate by evaporation.

4. Separation of the iron and aluminum by continuous ion exchange chromatography using gradient elution.

5. Precipitation of hydrous aluminum oxide which can be sintered to yield anhydrous alumina.

All of these methods should be capable of producing materials suitable for producing aluminum metal by electrolytic methods. Other product options are possible utilizing conventional hydrometallurgical techniques.

MARKETABLE EXTRACTED MATERIALS

The end products from some of the recovery processes include, as follows:[39]

Lime-Soda Sinter: Fe, Alumina, Cement
Salt-Soda Sinter: Fe, Alumina, MnO_2, TiO_2, Silica Gel
Acid Leach: Fe, Alumina, MnO_2, TiO_2
Calsinter: Fe, Alumina, MnO_2, TiO_2, Cement

TVA SUPPORT OF PROCESS DEVELOPMENT

TVA will be cooperating with Mineral Gas Company, Inc. (MGC) and the City of Lawrenceburg, Tennessee, in the construction and operation of a one ton per hour pilot plant to study the technical and economical feasibility of the MGC process discussed above.[41]

MGC has also proposed to build an alum extraction facility at the Bull Run Steam Plant using another process.[41]

ECONOMICS

No information was available on the MGC extraction process in the literature. Murtha and Burnet project that for a 1000 ton per day alumina output, fly ash could be processed via the HiChlor process for an 8% return on investment even if fly ash were purchased at $6/ton.[40]

Table 8[39,42] presents the estimated income per ton of alumina for several processes as presented by ORNL.

Table 8. ESTIMATED INCOME FROM MINERAL RECOVERY

Process products	Production (10^3 tons/year)	Income (\$/ton Al_2O_3)	Income (\$ 10^6/year)
Lime-soda sinter			
Iron	110	15.8	3.29
Alumina	208	155.0	32.30
Cement	1526	(322.1)	(83.95)
		170.8	35.59
Salt-soda sinter			
Iron	149	16.1	3.49
Alumina	217	155.0	33.61
MnO_2	2.6	2.4	0.51
TiO_2	15.3	37.5	8.12
Silica gel	227	(292.7)	(63.47)
		211.0	45.73
Nitric acid			
Iron	138	21.9	3.45
Alumina	157	155.0	24.27
MnO_2	1.8	2.0	0.32
TiO_2	5.8	19.8	3.10
		198.7	31.12
Calsinter			
Iron	144	16.5	4.31
Alumina	261	155.0	40.39
MnO_2	1.5	1.1	0.29
TiO_2	13.9	28.2	7.35
Cement	1550	(327.2)	(85.26)
		200.8	52.34
Bayer			
Alumina	350	155.0	54.25

The process may produce salable materials from fly ash in addition to alumina, some of them in substantial quantities. Cement and silica values are excluded from the totals because the volume of production is so large that market conditions could be drastically affected. Some of the plants could sell Portland Cement at reduced prices, some at prices near present values, while other plants use different processes which do not produce cement.[39]

For these calculations, the following selling prices were assumed: iron oxide pellets, \$30/ton; iron oxide powder, \$5/ton; alumina, \$155/ton; manganese dioxide, \$200/ton; titanium dioxide, \$530/ton; cement, \$55/ton; and silica gel, \$280/ton. The possibility of recovering other metal values, such as magnesium, exists for the salt-soda or Calsinter processes but has not been explored. No account was taken for reduction in disposal cost.[39]

Table 9[39,42] presents a summary of estimated annual operating costs, capital costs, and income for five processes. If cement can be sold, some processes are economically viable while others are not. Other processes, such as the salt-soda process, appear to be economically attractive. However, the costs for nitrate cleanup, which could be significant, were not included in either the salt-soda or the acid-leach process.

The capital costs of the processes include equipment facilities, engineering, contractor's fee, construction, interest, contingency, and working capital. These costs show that, although the Calsinter process may be the most economical on the basis of alumina produced, it requires a high capital investment. Cost figures for this type of estimate are useful in predicting relative costs of similar processes. All of these processes show economic potential and deserve further study and development.[42]

Table 9. ESTIMATED ANNUAL OPERATING COSTS, CAPITAL COSTS, AND INCOME

	Lime-soda	Slat-soda	Nitric Acid	Calsinter	Bayer
Operating costs ($/ton alumina)					
Raw materials	118.70	85.01	55.17	56.83	34.72
Utilities	56.76	30.32	39.86	65.11	22.55
Labor ($25,000/man-year)	4.80	4.61	6.39	4.41	3.00
Maintenance (10% of fixed cost)	92.74	30.44	37.04	27.62	25.72
Taxes and insurance (2% of fixed cost)	5.94	6.08	7.40	5.52	5.14
Depreciation (5% of fixed cost)	14.88	15.22	18.52	13.82	12.86
Total	230.82	171.68	167.38	173.31	103.99
Income from products ($/ton alumina)	170.80	211.00	198.70	200.80	155.00
Capital Costs					
Total capital for plant ($ 10^6)	62	66	58	72	90
Capital cost per annual ton of alumina ($)	297	304	370	276	257

Section 6

FLY ASH AND MAGNETITE RECOVERY

INTRODUCTION

A review of the literature indicated that Minnick in 1961 developed a procedure for magnetic ash separation that was used for concrete addition (43). In 1962, Joppa received a patent for magnetic fractionation of fly ash for use in coal preparation (44). A facility, which is presently not in operation, was built at Lakeview station of Ontario Hydro to remove the magnetite fraction from fly ash (45).

Few industrial installations have been built for magnetic recovery; and the only high volume installation in the U.S.A. to date is at Penn Virginia Materials Corp., in Cleveland, Ohio. This facility is now closed. The fly ash was separated magnetically dry on a series of three permanent magnet rotary separators and was then air classified. About 800 tons of magnetic fractions were removed per month and 60% of this material (≅40 micron size) was marketed as fine grade magnetite (43-47).

Researchers at Iowa State were the first to examine the use of the separated magnetic fraction of fly ash as a substitute for commercial magnetite in coal washing (46, 47) by using a device similar to that devised by Minnick (43). The Iowa State researchers (46, 47) found that 10-15% by weight of bituminous coal fly ash may be recovered as a magnetic fraction. The particles were spheroid in shape (commercial magnetite is angular) and 65-85% by weight passed a 325 mesh (44 micron) screen (this is similar to commercial magnetite). It is recommended that further processing via ball mill grinding and washing be conducted to remove the clay-like materials. The density of the ground and washed material was 3.5 g/cm^3, whereas commercial magnetite has a density of 4.7 g/cm^3. The viscosity of ground and washed magnetic fractions was lower than that of commercial magnetite and resulted in lower mixing energy requirements for stirring. Also, ground and washed magnetic fly ash fractions settled slower than commercial magnetite samples indicating that the magnetic fraction was more stable. Finally, the Iowa State researchers found that a ground and washed magnetic fraction was a good heavy medium material capable of washing coal.

HISTORY OF TVA INTEREST

TVA has initiated a research program related to magnetite recovery for coal washing. Phase I has begun and involves investigation of the economic and efficiency limits on the percent of magnetite that can be recovered from coal ash. Phase II will evaluate whether the magnetite fraction can be used in a heavy media coal cleaning process. Phase III will involve a technical and economic comparison of the magnetic fraction to commercial grade magnetite. Phase III intends to design, construct, and operate a magnetic separation facility on coal ash. The project is to be completed by January 1982 (41).

The long term need for the magnetic fraction can be projected to the TVA system. A coal cleaning facility is already being constructed at Paradise Steam Plant and it will process 2000 tons per hour. Assuming 1.5 lb. magnetite per ton of coal and an availability factor of 0.85, this one facility will require 8000 tons of magnetite per year. Iowa State (47) estimates that magnetite is worth between \$70-100/ton. Therefore, the Paradise coal washing facility could spend between \$600,000-\$800,000 per year to buy magnetite. TVA estimates that a fly ash magnetite recovery facility could be built at Paradise for \$250,000 (to generate 8000 ton/year magnetite). Excluding operating costs, this could save \$310,000-550,000 per year in commercial magnetite costs (41).

The general impact on the TVA region can be indicated by comparing estimated national coal cleaning demands with coal burned. For example, in 1979, about 500 x 10^6 metric tons of coal was burned in the USA. In 1985, this number could be 700 x 10^6 metric tons. It is estimated that by 1985, 365 x 10^6 metric tons of coal will be cleaned in the USA or roughly (365/700) 50% of that burned (47). TVA was burning, in 1975, 35.1 x 10^6 tons. If it is assumed that this tonnage holds constant through 1985 and if 50% is cleaned, then at a minimum 17.55 x 10^6 tons could be expected to be cleaned per year in 1985. At \$100 per ton for magnetite, and at 1.5 lbs. magnetite/ton, this could cost TVA \$1.32 x 10^6 annually to purchase magnetite.

Section 7

SINTERED FLYASH AND LIGHTWEIGHT AGGREGATES

Almost any material can be obtained with the required particle size and grading, provided it has the required strength and can be used as an aggregate for concrete provided it does not contain any substance liable to lead to unsoundness or to react in a harmful way with the cement.[1] Aggregates can be classified by weight as heavy, normal, or lightweight. Normal weight aggregates have a specific gravity of about 2.6, while heavy-weight aggregates have a specific gravity that is greater than 2.8. Light-weight aggregates have a specific gravity of less than 2.4.

The unit weight of concrete can be effectively controlled by the type of aggregate used.[51] Concrete with a weight of less than 115 lbs/cubic ft. is classified as a lightweight concrete. Lightweight concrete is produced by using various types of lightweight aggregates that are either natural or artificial or by keeping the fines out of the mix design.

The advantages of having a lightweight, structural concrete are based on the difference in weight between that and normal concrete. Lightweight structural concrete provides flexibility in designing longer spans, larger floor areas, added height or simpler foundations.

Many types of lightweight aggregate can be used in producing a lightweight structural concrete. These include: expanded slag; sintered shale, clay or flyash; and kiln expanded shale, clay and slate. Other lightweight aggregates, such as vermiculite and pumice, produce only low to moderate strength concrete because when the aggregate is below a certain density, the attained 28 day compressive strength is usually less than 2500 psi.

Producing lightweight aggregate from slate, shale, clay, or flyash requires either a sintering process or a heat expanded process. When certain clays, shales, and slates are heated to 1300-1400°F, they expand as a result of the formation of gas within the material. This develops a cellular structure of lower density.

For flyash, a lightweight aggregate can be produced by sintering. Usually the flyash is wetted and formed into pellets. The pellets are then placed on a grate in a firing chamber at about 2600°F. At this temperature the pellets soften and agglomerate into larger particles. The internal structure of the sintered flyash is filled with voids caused by evaporation of the pellet water and by the combustion of the residual carbon in the flyash. The sintered flyash is then cooled and crushed to desired sizes.

The carbon content of the flyash plays a large role in the sintering process as a source of heat during combustion. If the carbon content of the flyash falls below 4%, it is probably necessary to add pulverized coal to the pellets before sintering. If the carbon content is more than 6%, it may be necessary either to mix it with ash with a lower carbon content, or to fire the carbon and use an external source of heat. This is important because the sintering process must be closely controlled. The production of a suitable lightweight aggregate from flyash also appears to be a function of the size of the particles of the flyash before sintering.[48]

A number of facilities have been built for producing lightweight aggregate from flyash; however, at this time only a few are in operation.[3] Major problems include deficiencies in design, excessive wear, as well as the quality of the flyash being sintered.

The facilities that are currently operating in the U.S. are apparently not able to market the product for a profit. This fact is due in large part to institutional barriers to the use of flyash as a lightweight aggregate. Predictions that demands for lightweight aggregate will increase are based on the adoption of codes like those in Europe which allow the use of lightweight concrete and the use of sintered flyash.

Since sintered flyash is stable, easily handled and transported, it appears that the best place for a lightweight aggregate plant is next to a power facility. This would mean that any storage facilities could be in terms of sintered flyash instead of flyash. In addition, the handling of flyash would be minimized.

TVA has indicated that the Bull Run Steam Plant has been considered for a lightweight aggregate facility; however, at this time no serious plans have been made.

Section 8

FLY ASH UTILIZATION IN WASTE WATER TREATMENT

FLYASH APPLICATION IN WASTEWATER TREATMENT

Numerous researchers have evaluated the use of fly ash in aspects of wastewater treatment. These applications and their present problems with potential field scale systems will be discussed.

Deb, et al., studied the removal of COD from wastewater using fly ash. COD removal decreased after 10 minutes of contact time. It was found that 50 mg/l of activated carbon was as effective as 1000 mg/l of fly ash. Above 3000 mg/l, COD removal became independent of further flyash addition.[62]

Eye and Basu studied COD removal as well as sludge conditioning. COD removal decreased after 10 minutes contact time. With an initial COD of 60 mg/l and fly ash concentrations varying from 778-2570 mg/l, removals ranged from 15-40% and averaged about 30%. The authors project that 50-80% cost savings can be achieved via use of lime plus fly ash and fly ash alone as wastewater sludge conditioning chemicals.[63]

In a study by Tenney and Echelberger, fly ash was evaluated for these possible applications: lake restoration, sludge conditioning, and treatment of acid mine drainage. In studying fly ash addition to eutrophic lake waters, phosphorus and organic matter were removed. Organics (65-10%) were adsorbed; and it was surmised that due to extraction of lime and gypsum from the fly ash, phosphorus was precipitated. Dry, unreacted fly ash was more effective than washed fly ash. In the studies on sludge conditioning at greater than 50 grams/l, fly ash improved dewaterability and increased fuel value. The authors also found fly ash at greater than 100 grams/l to be effective in neutralizing acid mine drainage.[64]

Chu, et al., studied the capability of fly ash to remove a copper-ammonia complex which is discharged to ash ponds. It was surmised that copper is both adsorbed and precipitated by alkaline fly ash. Copper adsorption to fly-ash is dependent upon the amount of flyash added, up to 40 grams/l. Removal ranged from 94-99%.[65]

Finally, Gangoli, et al., studied the removal of heavy metals (from 3-100 mg/l) from aqueous solutions with fly ash. The following metals were removed fairly successively using as high as a 40 grams/l fly ash dose: Al^{+3}, Cr^{+3}, Mn^{+2}, Fe^{+3}, Ni^{+2}, Cu^{+2}, Zu^{+2}, Zn^{+2}, Cd^{+2}, Sr^{+2}, Pb^{+2}, $Cr_2O_7^{-2}$. Hg^{+2} was not effectively removed. Experiments indicated that prior acid treatment of fly ash was detrimental to metal removal. The authors proposed the following mechanisms for metal removal:

> Precipitation occurs at high pH probably as metal hydroxides.
>
> Cr anion is removed by reduction of Cr^{+2} to Cr^{+3} or by ion exchange.
>
> Adsorption is probably due to the presence of silica and alumina available in flyash.[66]

Although in some respects, fly ash addition to wastewater and sludge for metals, organics, phosphorus, neutralization benefits, and dewatering improvements, has been demonstrated, there are three problems that need to be addressed as well.

First, flyash has exhibited the ability to desorb heavy metals upon water contact.[67] Several authors have evaluated this effect.[62, 63, 64] With a future emphasis on priority pollutants, this may create problems in utilizing fly ash to aid wastewater treatment.

Second, if fly ash is added to the wastewater then the ash will ultimately end up in the sludge. Given concerns addressed to more proper management of solid wastes, this could present a problem because the sludge could become a hazardous waste following fly ash addition.

Third, most fly ash is not generated near a wastewater plant. The logistics of handling and economics of use would need to be studied.

SCRUBBER SLUDGES

Fly ash is used in some stabilization processes to aid pozzolanic reactions or to serve as a fly ash disposal technique. It is estimated by one commercial vendor, IU Conversion System (IUCS), that by 1982, 2.5×10^6 tons of ash will be used annually in that vendor's stabilization process, the Poz-O-Tec^R process.[70] This represents the largest fly ash utilization by any commercial vendor. Existing IUCS operations or those under contract with utilities are shown in Table 10.

The Poz-O-Tec material is formed by the addition of lime, flyash and other materials to FGD sludge to accomplish fixation. The flyash to sludge ratio is approximately 0.5 : 1, although a 1:1 ratio can be achieved. The fly ash serves as the pozzolan for the reaction. The largest installation in operation is at Columbus and Southern Ohio Electric Compan's Conesville Station and is designed to treat FGD sludge and flyash from two units totalling 830 MW.

Dravo has also patented a fixation process through the addition of Calcilox^R which is a cementitious product obtained from blast furnace slag. Flyash may or may not be added to the mixture, but in this fixation process, flyash is not a necessary ingredient for accomplishing the reaction. At the Bruce Mansfield Plant operated by the Pennsylvania Power Company, flyash and FGD wastes are treated from two units with a capacity totalling 1834 MW.

Table 10

PRESENT AND PLANNED IUCS INSTALLATIONS AS OF November 1, 1979

	Station/Unit(s)	MW
Big Rivers Electric	Green 1, 2	480
Central Illinois Public Service	Newton 1	615
Cincinnati Gas & Electric	East Bend 2	600
Columbus & Southern Ohio	Conesville 5, 6	800
Commonwealth Edison	Powerton 51	450
Duquesne Light	Elrama	500
Duquesne Light	Phillips	400
East Kentucky Power Coop	Spurlock 2	500
Hoosier Energy	Merom 1, 2	980
Indianapolis Power & Light	Petersburg 3, 4	1060
Lakeland Utilities	McIntosh 3	350
Louisville Gas & Electric	Cane Run 4, 5, 6	670
Louisville Gas & Electric	Mill Creek 1, 2, 3, 4	1580
Public Service of Indiana	Gibson 5	650
Southwestern Electric Power	H. W. Pirkey 1	720
Texas Municipal Power	Gibbons Creek 1	410

Source: FGD Sludge Disposal Manual, Second Edition, Michael Baker, Jr., Inc. EPRICS-1515, September 1980.

Other propietary stabilization/fixation processes include ones by American Admixtures, Inc. and the Stablex Corporation. The Sealosafe^R process patented by Stablex is commercially available in Europe and combines portland cement or cement dust, flyash, industrial waste, and sometimes lime, other companies also offer cement processes, but commercial applications have not been made for flyash utilization.

Physical stabilization of scrubber sludge has been proposed and received limited application. At the Southwest Station of Springfield City Utilities, FGD sludge is processed by thickening, followed by vacuum filtration. The filter cake is then blended with flyash. The mixture is achieved with a non-alkaline flyash hence a pozzolanic reaction is not made, and care must be taken to keep the disposed material dry.

Section 9

FLY ASH AND SANITARY LANDFILL LINERS

Fly ash can be used for improving the properties of the soils used to line cells in sanitary landfills and the properties of the soil used for the final cover. TVA has conducted several tests to determine the conditions under which fly ash can be used as either a soil extender or amender. Public Law 94-580 directs the U.S. Environmental Protection Agency to determine the regulations associated with the approval and operation of sanitary landfills. Because of the concern for leachate from sanitary landfills polluting aquifers or nearby surface waters, the current promulgated regulations require that location of landfills, along with the operation, must insure that no appreciable impacts occur to surface or groundwaters. This means that whenever ground waters could be impacted, the lining of the landfill must be close to impervious. In addition, to reduce the potential for leachate, the surface must be graded and swelled to remove any large potential for infiltration. EPA has issued criteria for the protection of groundwater which should be consulted in this regard.

Utilizing fly ash in both lining soil material and covering soil material can help in attaining the desired properties. In 1972 and 1978, TVA blended ash to soil samples from landfills of Coffee, Scott, and Sumner counties in Tennessee to determine whether ash can be easily used and to what degree the ash amended soil can be impervious. For the TVA studies, the ash was taken from the spoil area at the Gallatin and Kingston Steam Plants. Both fly ash and bottom slag were used in the study. The sizing of the two ashes are given in Tables 11 and 12.

The soils from each of the two landfills were blended with both types of ashes under several conditions of moisture. When the soil was moist and mixed with the fine fly ash, the absorption rates were slow for ranges of soil to ash of 1:1 to 1:3. When similar soil was mixed with the slag, the absorption rates were medium to rapid under the same mixture ratios. When the soil moisture was increased about 4% above normal moisture to represent wet weather conditions, the soil and flyash blends were hard to mix. When the soil was mixed with wet fly ash or a mixture of wet fly and bottom ash, the absorption rates were slow for the soil to ash ratio of 1:1. The results are given in Tables 13, 14 and 15 for the tests made.

It appears that when the soil has a normal moisture content, it is feasible to mix either fly ash or a mixture of fly and bottom ash with the soil to reduce permeability. The easiest blending ratio to produce is a 1:1 under normal operating conditions according to TVA results.

Table 11. SANITARY LANDFILL LABORATORY STUDY USING KINGSTON POWER PLANT ASH

	Particle Sizes - Percent Passing		
	1-Inch Sieve	No. 4 Sieve	No. 200 Sieve
Ash type: Fly ash (fine bottom)	100	92	4

Plasticity: None
Natural moisture content (sample): 27%
Compacted wet unit weight: 95 pcf
pH: 4.8

	Particle Sizes - Percent Passing		
	1-Inch Sieve	No. 4 Sieve	No. 200 Sieve
Ash type: Coarse ash (slag)	100	81	32

Plasticity: None
Natural moisture content (sample): 14%
Compacted wet unit weight: 115 pcf
pH: 2.8

Table 12. SANITARY LANDFILL LABORATORY STUDY USING GALLATIN POWER PLANT ASH

	Particle Sizes - Percent Passing	
	No. 4 Sieve	No. 200 Sieve
Ash type: Fly ash (fine bottom)		
Plasticity: None		
Natural moisture content (sample): 55%	100	90
Compacted wet unit weight: 90 pcf		

	Particle Sizes - Percent Passing		
	1-Inch Sieve	No. 4 Sieve	No. 200 Sieve
Ash type: Coarse ash (slag)	100	70	20
Plasticity: None			
Natural moisture content (sample): 12.5%			
Compacted wet unit weight: 120 pcf			

Table 13. SANITARY LANDFILL LABORATORY STUDY FOR COFFEE COUNTY

	Particle Sizes		
	Sand %	Silt %	Clay %
Soil type: Fat clay	20	40	40

Plasticity: Medium to high (plasticity index 33)
Natural moisture content (sample): 28%

Blend Ratios (By Volume)		Rate of Absorption
Soil:	Fine Ash*	
1	1	Slow
1	2	Slow
1	3	Slow
Soil:	Wet Fine Ash	
1	1	Slow
Wet Soil:	Fine Ash**	
1	1	N.A.
Soil:	Coarse Ash*	
1	1	Medium
1	2	Rapid
1	3	Rapid
Soil:	Wet Coarse Ash	
1	1	Medium
Wet Soil:	Coarse Ash**	
1	1	N.A.
Soil:	Mixed Ash*	
1	1	Slow

---

*Soil and ash tested at natural moisture contents.

**The wet soil has poor blending characteristics.

Table 14. SANITARY LANDFILL LABORATORY STUDY FOR SUMNER COUNTY

	Particle Sizes		
	Sand %	Silt %	Clay %
Soil type: Medium clay	15	40	45

Plasticity: Medium (plasticity index 24)
Natural moisture content (sample): 25.5 percent

Blend Ratios (By Volume)		Rate of Absorption
Soil:	Fine Ash*	
1	1	Slow
1	2	Slow
1	3	Slow
Soil:	Wet Fine Ash	
1	1	Slow
Wet Soil:	Fine Ash	
1	1	N.A.
Soil:	Coarse Ash*	
1	1	Rapid
1	2	Rapid
1	3	Rapid
Soil:	Wet Coarse Ash	
1	1	Medium
Wet Soil:	Coarse Ash**	
1	1	N.A.
Soil:	Mixed Ash*	
1	1	Slow

---

*Soil and ash tested at natural moisture contents.

**The wet soil has poor blending characteristics.

Table 15. SANITARY LANDFILL LABORATORY STUDY FOR SCOTT COUNTY

	Particle Sizes			
	Gravel %	Sand %	Silt %	Clay %
Soil type: Medium clay	16	16	29	39

Plasticity: Medium (plasticity index 25)
Natural Moisture content (sample): 21.7%

Blend Ratios (By Volume)		Rate of Absorption
Soil:	Fine Ash[*]	
1	1	Medium
Soil:	Coarse Ash	
1	1	Fast
Soil:	Mixed Ash	
1	1	Slow
Wet Soil:	Mixed Ash[**]	N.A.

---

[*] Soil and ash tested at natural moisture contents.

[**] The wet soil has poor blending characteristics.

The use of fly ash in landfills depends on the accessibility of a good source of ash as well as the overall need. In addition, the use is also a function of weather conditions, since blending cannot be easily done when soil moisture is high. One of the nicest features of this alternative is that the ash can be utilized when it is wet. In fact, this means that ponded ash could be used when most alternatives require that the ash be dry. One point should be mentioned here: the potential for utilization is a function of specific site characteristics and accessibility. At this time, the utilization of fly ash as a material for landfill liners remains an alternative that looks good if the fly ash is not being put to alternative use.

Section 10

CENOSPHERES

BACKGROUND AND DESCRIPTION

A small portion of fly ash typically consists of small microscopic hollow spheres referred to as cenospheres. These spheres are frequently referred to as floaters, resulting from the property that they exhibit in ash settling ponds; all cenospheres do not, however, float. The uniqueness of cenospheres is their light weight, coupled with their ability to withstand hydrostatic pressures in excess of 100,000 psi.[30] They are relatively non-grindable and inert when cleaned. The floaters tend to have tiny pinholes in their walls which decrease their strength in comparison to "sinker" cenospheres. Also, cenospheres are able to withstand temperatures up to 2000°F making them a desirable fire insulation material.

Although the floaters may be only a small percentage of the total fly ash, the "sinkers" may be a relatively large portion of the total ash.

Zeeuw and Abresch[32] reported that Northern States Power Company's fly ash from a pulverized fuel plant contained 50-70% cenospheres. The wall thickness of the floaters was found to be 5-8% of the diameter, whereas the remainder of the cenospheres (sinkers) had wall thicknesses of up to 30% of the diameter of the spheres and higher strengths. Typically, the floaters are skimmed and collected from fly ash sluice ponds while the sinkers and floaters are collected in a dry separation process.[30] They are frequently separated by size into the "minus to 5 micrometer," "5-50 micrometer," and "greater than 50 micrometer" ranges dependent on their potential use.

Chemically, the cenospheres are composed of SiO_2, Al_2O_3, Fe_2O_3, and traces of other compounds. Ashby and Carroll[31] reported on Australian cenospheres which were 55% SiO_2, 36% Al_2O_3, 2.2% Fe_2O_3 and 1.5% K_2O. At Northern States Power Plant (Minnesota) the content was 52% SiO_2, 39% Al_2O_3, 1% Fe_2O_3, and 5% K_2O.

A series of tests were conducted by Colorado School of Mines Research Institute on a TVA total fly ash sample.[30] Ceno Science Research, Inc., separated the material to be tested into magnetic material, carbon black, floater cenospheres (specific gravity ≦1.0), and cenospheres with specific gravity ≧1.0. These later spheres were then beneficiated into plus 50 µm, minus 50 plus 5 µm, and minus 5 µm products. The results were as follows:

1. The fly ash can be separated into desired plus 50 µm, 5 to 50 µm, and minus 5 µm cenospheres by wet methods.

2. Removal of iron to an acceptable level, 2% or less, by low-intensity magnetic separation was not possible.

3. Carbon black removal to the desired level of 1.0% or less was possible using froth flotation.

4. Soluble salts in the minus 5 µ cenospheres were removed to a level of 0.02% by washing.

5. The specific gravity of both the minus 50 plus 5 µ and minus 5 µ products was 2.48.

6. The specific gravity of the floating cenospheres was 0.74.

7. The pH of the minus 5 µm pulp was 6.0.

8. The products from the total fly ash sample had the following weights and distribution:

Product	Weight (g)	Distribution Weight (%)
Floating Cenospheres	32.6	0.2
Magnetic Concentrate	919.5	4.3
Magnetic Cleaner Tailing	1,513.4	7.1
+50 µm	983.0	4.6
5 to 50 µm	15,892.8	74.1
-5 µm	2,070.5	9.7
Total	21,411.8	100.0

9. The 5 to 50 µm cenospheres had the following chemical analysis: Na_2O, 0.3%; MgO, 1.3%; Al_2O_3, 28.2%; SiO_2, 49.5%; SO_3, 0.5%; K_2O, 0.2%; CaO, 1.1%; TiO_2, 1.1%; Fe_2O_3, 6.0%.

10. The minus 5 µm cenospheres had the following chemical analysis: Na_2O, 0.3%; MgO, 1.2%; Al_2O_3, 25.4%; SiO_2, 49.1%; SO_3, 0.3%; K_2O, 0.4%; CaO, 1.0%; TiO_2, 1.1%; Fe_2O_3, 5.4%.

APPLICATIONS

At the present time several markets exist for cenospheres, dependent on the characteristics of the spheres. Areas under evaluation include:[32]

a. plastic extenders
b. aluminum
c. paints
d. tapes
e. sands
f. insulation
g. foams
h. coatings
i. rubber compounds
j. sprays
k. fire proofing

Turner[30] reported a successful application of cenospheres as a filler in flexible polyurethane foam where up to 48% by weight was utilized. The market involved the use of foam in products such as carpet padding, mattresses, and cushions. Carpet industry officials have expressed considerable interest in this type of rebound padding. Since the carpet padding industry utilizes close to one billion pounds of rebounding padding per year and rebound material availability is decreasing, a strong market for cenospheres exists.

Studies have also been conducted on the use of cenospheres as a paint filler. The potential advantages of the less than 5 µm fraction are the wearing capability, retention of high gloss under corrosion, and weathering tests. It was estimated that the primary use of minus 5 µm cenospheres would be in the paint industry.[30]

Investigations are currently being conducted[30,32] on the use of cenospheres as a plastic binder. In Australia, Ashby, *et al.*[31], reported that the main use of cenospheres was in plastics because of the light weight and low resin demand; cenospheres were found to require less resin per unit volume of product than talc.

Ashby, *et al.*[31], also studied the use of cenospheres as a concrete additive for replacing sand. When compared to a blended cement/sand cement (1:1.8 by volume) which had 7 day and 28 day compressive strengths of 2465 psi and 6160 psi, a mixture of 1:1:1 cement/sand/cenospheres had 7 day and 28 day compressive strengths of 2175 and 5438 psi. A mixture of ½ cement/cenospheres had 7 day and 28 day compressive strengths of 1810 and 4495 psi. Although strength was reduced by the addition of cenospheres, it was concluded that there was still a potential use for the cenospheres in lightweight construction such as for ferro-cement boat construction.

Section 11

USE OF FLYASH IN AGRICULTURE

INTRODUCTION

Previous sections of this report have indicated that flyash may be an important source of specific elements required as nutrients in the growth of plants as well as animals. It has been shown that although the bulk of flyash consists of SiO_2, Fe_2O_3, Al_2O_3 (commonly greater than 85%), fly ash also contains various amounts of elements considered to have nutrient and/or liming value when used as a soil conditioner. Unfortunately, while many useful nutrients may be present, some elements in specific flyashes may be present in concentrations that could potentially cause an undesirable side effect due to their toxicity to vegetative matter and/or foraging animals. EPA has issued criteria concerning the application of solid waste to land used for the production of food crops.

The properties of flyash have been summarized in Section 2. One of the most significant properties is the property of many fly ashes to have a liming value, a quality very important in strip mined areas and in soils of an acidic nature. Furr, et al.[5], showed that for flyash obtained from 21 states (23 sites), 16 of these had pH values in excess of 7.0 with a maximum of 11.8. In general, the lignite coals have high pH due to the presence of substantial concentrations of alkali oxides. Ray and Parker[4] have summarized data from which it was concluded that significant variations in CaO, MgO, Na_2O and K_2O exist within coals found in the USA. Fail and Wochok[9] reported the neutralizing power of bituminous coal to range from 15 to 200 tons of ash equivalent to one ton of lime. Phung, et al.[10], in a study on Western flyashes, concluded that many western coals were strongly alkaline and that Pb, Co, Ni, Cd, Mo, Se, and As existed in concentrations higher than in most mineral soils. However, due to the higher pH of the flyashes, the solubility of these trace elements was reduced.

FLY ASH AS A SOURCE OF NUTRIENTS*

As a Source of K and P

Total K content of fly ash from 21 power plants in the U.S. ranged from 0.15 to 3.47%. Eight of the eastern sources and one from Minnesota were evaluated in a plot experiment as sources of K for corn grown on acid Davidson clay loam by Martens, et al.[11] Dry matter and K uptake were increased significantly, presumably as a result of the liming effect of the fly ash on the acid soil. Concentrations of K in the corn were not increased appreciably by eight of the fly ashes applied at rates to supply 158 and 474 mg of K/plot. The Minnesota source applied at lower K rates had a greater liming effect and resulted in higher K concentrations and uptake by corn.

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*Section taken from TVA report written by G.L. Terman, Agronomist, Soils and Fertilizer Research Branch, National Fertilizer Development Center, TVA.

Although elemental composition of fly ash is quite variable, it usually contains higher concentrations of essential plant nutrients (except N) than do soils.[12,13,14]

Martens[15] found that P deficiency of corn grown in a pot experiment on Landisburg silt loam was corrected by application of 210 mg of P as a soluble phosphate, but only partially by the same amount of P in fly ash (125 g/pot containing 0.17% P) from Maidsville, West Virginia. Soil pH was increased from 5.6 to 7.2 by this application, which may have reduced P availability.

As a Source of S

Elseewi, et al.[16] found the 0.4% S in ash from a western U.S. coal was readily available to alfalfa (Medicago sativa L.) and other crops.

As a Source of B and Other Micronutrients

Total B concentrations in fly ash (Table 4) ranged from 10 ppm to 600 ppm.[5] Fly ash samples from 11 TVA power plants ranged in total B from 120 to 480 ppm; water-soluble B increased with total B (r = 0.96). An average of 72% of the total B was water-soluble (TVA data).

Mulford and Martens[17] evaluated the availability of the B in three fly ashes containing 319, 415, and 618 ppm of total B for alfalfa grown on Tatum soil. Availability of the B in fly ash was equal to that in borax. The higher rates of the Montanta fly ash (618 ppb of B) decreased yields, probably as a result of its liming effect which decreases availability of Mn and Zn. Soil pH was increased from 5.9 to 7.7 by the highest rate (21.6 mg of B, or 350 g of fly ash/pot of 2.1 kg of soil). Plank and Martens[18] found that dissolution of B in hot water was a good index of crop availability of B in soil-fly ash mixtures.

FRESH VERSUS WEATHERED FLY ASH

As mentioned previously, most sources of fresh fly ash from the collectors are highly alkaline (pH 9-10) and contain varying amounts of soluble B. On contact of the alkali metal oxides with moisture, hydroxides are formed, which undergo further reaction with CO_2 in the air to form carbonates (pH 7.5-8.5). Thus, on exposure to moisture and air, initial toxicity to plants due to high alkalinity soon decreases.

Soluble B in fresh fly ash is also toxic to plant growth at disposal rates of application. If the fly ash is conveyed to drained waste pond sites, leaching by water will soon remove soluble B and reduce alkalinity. As a result, a ponded area will usually sustain vegetative growth within a year or two under natural rainfall in humid climates if needed nutrients (largely N and P) are provided.

Holliday, et al.[19], and Rees and Sidrak[20,21] suggested that fresh fly ash caused Al and Mn toxicity in plants. Holliday, et al.[22], however, concluded that B, rather than Al or Mn, was the toxic element.

FLYASH AS A SOURCE OF MULTIELEMENT SOIL AMENDMENT AND/OR ANIMAL RATION

Although the use of flyash as a source of nutrients has been studied rigorously, many of the earlier studies (1950-1975) did not review in depth the uptake of non-nutrient elements with potential toxic side effects. These earlier studies concentrated on the positive benefits of soil enrichment by flyash by addition of appropriate elements such as K, P, B, Mn, and Zn. Since 1976 several significant studies have been conducted to investigate the multielement uptake of (1) plants grown on fly ash amended soils[23,24], and (2) animals either fed rations containing fly ash[26] or fed food grown on flyash ammended soil.[25]

Furr, et al.[23], conducted a study in which 42 elements were determined in beans, cabbage, carrots, millet, onions, potatoes, and tomatoes grown on soil amended by addition of 10% by weight flyash. Thirty-two elements were present in higher total concentrations in the fly ash than in the soil. Thirteen elements were found to be in higher concentration in the edible portions when grown on flyash amended soil, compared to the control soils. Because of the 9:1 ratio of soil to flyash, there were only three elements for which the average ppm of the elements in the amended soil was increased by more than a factor of 2. (These were Arsenic, Selenium, and Molybdenum with relative increases in concentration of factors of 5.7, 6.5, and "unknown," respectively.) The data are presented for these three in Table 17. The uptake of both arsenic and selenium were significantly greater in some cases than the relative increase in concentration of the element in the soil.

A study was also conducted using a 5% flyash ammended soil. It was concluded that the uptake of Selenium was roughly proportional to the rate of application of flyash.[23] Ehlig[27] has noted that dietary Se concentrations necessary for preventing Se-deficient disease syndromes in livestock feed diets is between .02 and .10 ppm, and that above 5 ppm Se-toxicity occurs. Although the data in Table 16 are less than 5 ppm (1.9 ppm in the amended flyash), they are significantly greater than the level required to satisfy a Selenium deficiency. Further, Ehlig has shown that a thorough knowledge of both Selenium concentration and plant type is required since the Selenium uptake is affected to a measurable extent by the plant species.

In more recent studies, Stoewsand, et al.[24], have studied the uptake and response of Japanese quail fed wheat grown on flyash. In this study a winter wheat was grown to maturity on a deep bed of flyash, harvested, and fed as 60% of a complete diet to quail for 112 days. The wheat contained 5.7 ppm (dry wt.) of selenium, compared to .02 ppm for the control wheat grown on

Table 16. INCREASE IN MULTI-ELEMENT UPTAKE OF PLANTS GROWN IN FLY ASH AMENDED SOIL

	As			Se			Mo		
	Control	Ammended Soil	Ratio[b]	Control	Ammended Soil	Ratio[b]	Control	Ammended Soil	Ratio[b]
Beans	.01(c)	.2(c)	20	.02(c)	.47(c)	24	.9(c)	3.2(c)	3.5
Cabbage	.1	.2	2	.01	.95	95	1.0	2.2	2.2
Carrots	.01	.2	20	.00	.19	20	.2	.4	2.0
Millet	.2	1.0	5	.02	.90	45	.3	1.2	4.0
Onions	.1	.03	.3	.00	.30	30	.7	.4	.6
Potatoes	.1	.1	1	.01	.49	49	.2	.6	3
Tomatoes	.1	.1	1	.01	.20	20	.5	.8	1.6
Soil	2.9	13.9[a]	---	.3	16.8[a]	---	---	11.5[a]	---
			5.7			6.5			
		16.5[c]			1.95				

[a] Flyash before mixing at 9:1 soil to flyash;

[b] Ratio of flyash amended soil concentration to control soil concentration;

[c] ppm in amended soil.

soil. The tissues and eggs of the quail contained greatly elevated levels of selenium compared to the control quail. The average ppm (dry wt.) found in the quail fed flyash was 3.4, 4.4, 9.4, 11.2, and 3.9 ppm in the brain, heart, kidney, liver, and muscle, respectively; the control ppm levels were 0.8, 0.4, 1.4, 0.7, and 0.2, respectively. The primary effect of the increased selenium was to increase the egg shell thickness by roughly 7%. It was concluded that flyash high in selenium, but low in toxic elements, might be a desirable amendment to low selenium soils.

Furr, et al.[25], studied the uptake and elemental content of tissues and excreta of lambs, goats, and kids fed white sweet clover grown on flyash found to contain high concentrations of selenium, bromide, molybdenum, rubidium, strontium, and others. The harvested clover containing 66 ppm of selenium was fed as 23.5% of a dry pelleted ration to lambs and goats for 173 days. High concentrations of selenium were found in tissues, blood, goats milk, and excreta. In excess of 6.0 ppm was found in the goat's milk. Although no toxic effects were reported in the animals studied, it was stated that 0.5 ppm of selenium in milk is considered unsafe for human consumption. Molybdenum in liver, strontium in bone, and bromine and rubidium in animal tissues were also elevated in the animals fed the fly ash amended ration.

In a similar study by Furr, et al.[26], sheep, fed a 7.5% by weight of fly ash in pelleted rations (with a selenium concentration in the ration of 0.6 ppm), were found to be fairly resistant to the Se uptake compared to a control group. It was concluded that although no adverse effects were observed, the practice would appear to have limited value as a means of increasing selenium content in deficient animals.

DISCUSSION

Based on a review of the literature, it can be concluded that Se has been studied extensively. Both Arsenic and Molybdenum have been studied to a lesser extent. Although many factors such as application procedure, soil condition, plant species, and animal species have been found to cause significant variations in uptake of metals, it can be concluded that a key factor in determining the suitability of flyash as a soil conditioner or ration conditioner for any specific constituent is a complete analysis of all other constituents. In particular, a thorough knowledge of the ratio of the level of each constituent in the flyash amended soil to the original soil is necessary. In the studies reviewed, a significant increase in concentration of any constituent (generally greater than two) resulted in an observable increase in that constituent in the crops being produced and in the livestock fed those crops.

Furr and Parkinson[5] conducted a national survey of the fly ashes from 21 states in 1975-1976 in which 45 elements were evaluated for chemical content as reviewed in a previous chapter of this report. It is significant to note that the range of concentrations of elements varies widely from state to state as shown in Table 4. For many of the elements, the range is greater than 2 orders of magnitude. A brief comparison of these ranges with the typical soil used by Furr, *et al.*[23], reveals that at a 9:1 mixture of soil to flyash that As, B, Ba, Ca, Cd, Cu, Fe, I, Mo, Pb, Sb, Se, Sn, Sr, and U could potentially exist at concentrations greater than a factor of 2 times the concentration in the soil. Although only three elements were found in Furr's study with the particular ash used, sufficient evidence exists to indicate that a case by case evaluation might be required for determining the feasibility of flyash as an amendment to soil.

A final factor which further complicates the analysis of feasibility is that the trace elements generally are preferentially found in discrete size particles in the flue gas. As a result, the concentration of any given element may vary significantly. Kaakinen, *et al.*[8], compared the ash collected in the bottom ash centrifugal collectors, electrostatic precipitator, and wet scrubber for Public Service of Colorado's Valmont Station, Unit No. 5, near Boulder, Colorado. For example, selenium was found to be 1.9, 7.7, and 62 ppm for the coal, mechanical collector ash, and electrostatic precipitator outlet ash, respectively.

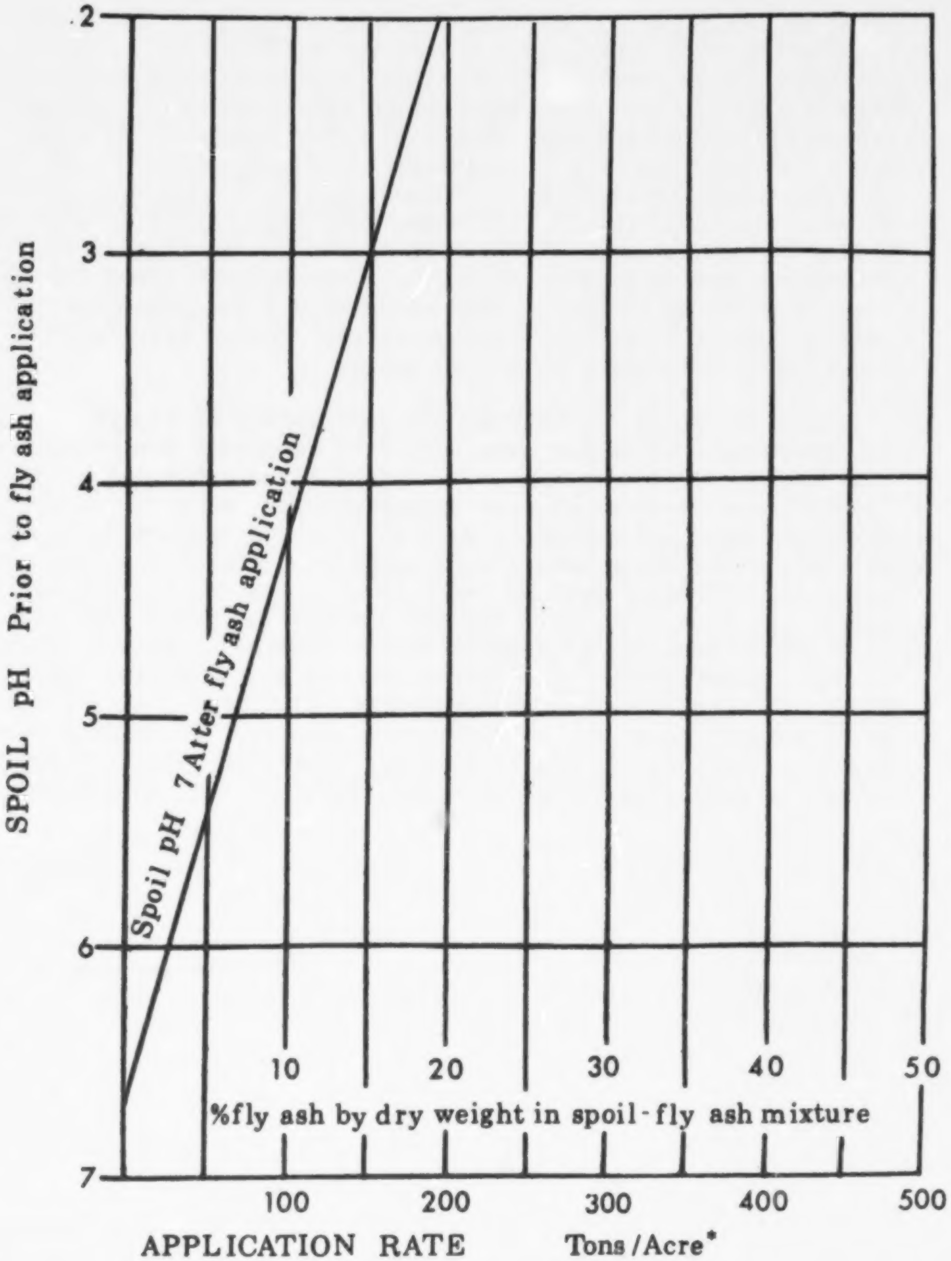
In conclusion, "the safe use of flyash in agriculture would therefore require careful and persistent monitoring of the complete elemental composition of flyashes, that of plants grown on them, and the tissues of foraging animals" (Furr, *et al.*[23]).

APPLICATION OF FLY ASH TO MINE SOILS

In recent years, studies have been conducted to determine if fly ash might be used as a soil amendment in highly acidic strip mine soils where vegetative reclamation is difficult. The acidic nature of strip mine spoil has generally prevented rapid reclamation due to nutrient deficiencies resulting from the low pH of the acid-mine spoils. The use of certain flyashes has been found to aid the revegetation. Experiments have shown that flyash mixed with mine spoils may raise the pH of acid soil as well as add additional calcium, magnesium, and other needed elements. Further, the flyash application may enhance the moisture retention ability, increase the air capacity, and improve soil texture.[10,28] However, flyash does not normally contain sufficient phosphorus or nitrogen; therefore, a fertilizer may be required. Although generally beneficial for vegetative reclamation, the negative aspects of flyash addition (i.e. boron toxicity, selenium toxicity of vegetative cover to foraging animals) must still be considered.

FLY ASH NEUTRALIZATION CAPACITY

The primary benefit of flyash application to acid mine spoils is the neutralization capacity of the ash. McLean, *et al.*[28], performed a series of labortory tests on various samples of strip mine spoils by mixing them with various percentages of flyash. For a flyash (pH = 10.6) the relationship between application rate required to neutralize to pH = 7 and the initial spoil pH is shown in Figure 8 illustrating typical application rates. Of several plants studied, it was noted that the neutralization capacity varied significantly. The "neutralization capacity" (NC) was measured in



spoil sample number

* To convert Tons/Acre to Metric Tons/Hectare multiply by 2.2416

Figure 8. Fly Ash Requirements to Raise Soil pH to 7

terms of the number of milliequivalents of H_3O^+ per 100 grams of flyash. For the Mitchell Power Plant flyash (pH = 10.7), the NC was 45; whereas for another plant's (Phillips Power Plant with a pH of 9.0) flyash, the NC was only 3. Thus, the flyash application rate required to neutralize an acid mine spoil would be approximately 15 times greater than with the pH = 10.6 ash. This represents a substantial increase in the cost of reclamation due to shipping costs of flyash. McLean, *et al.*[14], have also documented that the NC of a single source of flyash may vary significantly. For instance, the Mitchell Power Station NC was 9-99 at the 95% confidence level with 54 as an average over a 9 month period. It was further noted that the use of average spoil pH was not a good value to use for determination of the application rate of flyash; rather,the extreme low pH was preferred due to the logarithmic properties of the pH scale.

Keefer, *et al.*[29], studied the application of flyash, sewage sludge, and chicken manure to barren mine spoils to determine the effects of individual applications versus various mixtures of three additives. Application of flyash alone resulted in poor legume growth. Although pH was increased, the nutrients were not present. Both alfalfa and lespedeza ground covers grew well where all three wastes were supplied. Flyash combined with other waste materials increased soil pH and P levels, and decreased levels of toxic elements such as Al, Mn, Ni. Typical application rates used with success were 22.4 metric tons/ha, 27 tons/ha and 45 tons/ha of manure, flyash, and sewage sludge, respectively. The conclusion reached by McLean, *et al.*[28], and Keefer, *et al.*[29], was that flyash alone had no significant effect due to nutrient deficiencies; however, in combination with fertilizer it produced desirable results. Further, it was recommended that test plot studies should be conducted to determine the proper combination of the additives.

Section 12

MINERAL WOOL INSULATION

BACKGROUND

With increasing shortages of energy and price increases associated with home, office, and industrial heating and cooling, considerable emphasis is being placed on insulation. Mineral wool is a competitive insulation product. Making mineral wool from ash would result in decreased ash waste volumes and thereby decrease waste disposal problems.

Research conducted at the Coal Research Bureau (CRB), West Virginia University, from 1966-1970, indicated that it is possible to manufacture mineral wool insulation from bottom ash, from fly ash, and from limestone modified bottom ash and fly ash. At the time, however, energy costs did not make the alternative appear competitive.[74,75,76]

The primary raw material for conventional mineral wool production is waste blast furnace slag from the steel industry. Sometimes fluxing agents such as Ca and Mg salts are added to maintain proper chemical composition. The slag is generally heated in a coke-fired cupola furnace to a molten state (2600-2800°F). The slag is discharged to a concave metal wheel spinning at 1000-1500 rpm which forces the slag off the edge in thin sheets. Fine steam spray jets then cause the fibers to form. The fibers are collected and then either granulated and bagged or resin treated and pressed into batts. To use coal ash, it is recommended that a reverberating furnace be used rather than a cupola due to the small particle size associated with coal wastes.[75]

In general, the viscosity of the molten ash and the "temperature of critical viscosity" (TCV) determine whether a given slag can be used to manufacture mineral wool. TCV is defined as the point where the viscosity of the liquid begins to increase rapidly with a small decrease in the liquid temperature. Other conditions being the same, both fiber length and diameter will increase with an increase in slag viscosity. Conversely, if the viscosity is lowered below a given point, there will be an absence of fiber with only spherical solids being formed.[74,75]

Most manufacturers use the acidity modulus, usually referred to as the acid/base ratio (wt % SiO_2 + wt % Al_2O_3/wt % CaO + wt % MgO), of the raw materials as a guide in attaining the proper TCV. Generally, the ratio is maintained between 0.8 and 1.2. The addition of a limestone or dolomite flux in the proper proportion is generally used to adjust the acid/base ratio.[74,75]

The CBR studies investigated limestone, dolomite, and modified fly ash as fluxing agents.[74,75,76]

TVA has expressed an interest in producing mineral wool insulation from wet bottom ash generated at Allen and Paradise Steam Plants. Since both plants are wet bottom boilers, energy savings result from using molten slag tapped from the furnace as compared to having to remelt slag. The temperature of the molten slag must be raised in order to produce mineral wool. TVA has conducted bench scale and pilot scale work and found the process to be technically feasible.[77] At the present time, implementation has been halted due to the question of radioactivity associated with fly ash and bottom ash.[41]

QUALITY OF MINERAL WOOL

Table 17 presents a comparison of mineral wool production factors for the CBR coal ash studies and for the primary mineral level industry.[78] Table 18 presents characteristics of mineral wool made from coal and those of commercial mineral wool.[78] Table 18 summarizes slag for bituminous and lignite ash as well as for modified (limestone) ash.

Commercial wool is generally brown in color, whereas most of the other wools are lighter in color. Also, the average coal ash wool has a smaller fiber diameter than commercial wool. The corrosion characteristics are only slightly different. The quality of coal ash wool is similar to commercial wool.[78]

MARKET CONDITIONS

The mineral wool industry growth was from a sales value of \$100 x 10^6 in 1950 to \$500 x 10^6 in 1968.[78] In 1976, the industry sales volume was \$1335 x 10^6.[79] With rising energy prices, decreases in supply, and available tax credits, the national increase in insulation sales is a certainty. Since most commercial mineral wool is made from steel slag, if coal ash mineral wool can be economically competitive, the future demand could be met by coal ash mineral wool. Also, since fiberglass insulation is petroleum-based, coal ash mineral wool would provide an opportunity to reduce petroleum use. On a national basis, coal ash usage for insulation may reduce the cost of insulation due to the somewhat limitless resource base of ash.

Economics

The Coal Research Bureau presented the following advantages and disadvantages of using coal ash for mineral wool production:[75]

Advantages

(1) No mining costs are incurred as compared to use of wool rock.

(2) Little raw material preparation is required as compared to use of blast furnace slag.

(3) Raw materials costs are markedly reduced because fluxing agents are not required.

(4) Raw materials are available near virtually all major markets, thus minimizing transportation costs.

(5) Some forms of coal and ash wool retard corrosion of piping, thus reducing piping maintenance costs.

(6) High silica and alumina content of coal ash wool improve its insulating and heat duty properties as compared to other types of mineral wool.

Disadvantages

(1) Fine-particle size of coal ash required use of reverberatory furnaces for melting on a batch or semi-batch basis. Continuous cupolas, which are thermally more efficient, cannot be used.

(2) Due to color of the finished mineral wool, bituminous and anthracite ashes are not suitable for use in exposed surfaces (eg, acoustic tile). Lignite and sub-bituminous ashes are, however, suitable.

TVA estimated that a 4 ton per hour plant built at Allen Steam Plant could manufacture coal ash mineral wool insulation at $132 per ton. It was also indicated that the 1978 market price was $200 per ton.[77] TVA's cost estimate included capital amortization and operating costs.

Summary

Mineral wool insulation can be produced from coal ashes. Properties of coal ash mineral wool are similar to those of commercial wools. Research has indicated that not only bottom ash, but fly ash and limestone modified fly ash can be processed into mineral wool insulation as well. With a rapidly expanding demand for insulation, coal ash mineral wool can supplement the existing market, but it will not substitute for the existing commercial wools. In a study by TVA, coal ash mineral wool can be produced at a cost significantly below commercial wools.

Table 17. A COMPARISON OF MINERAL WOOL PRODUCTION FACTORS

	Industry	Coal Research Bureau
Raw Material	Wool rock-(calcareous sandstone or shale) or blast furnace slag + $CaCO_3$ + SiO_2	Coal-ash slag and/or flyash
Furnace	Cupola-water jacketed and/or reverberatory furnaces	Carbon arc
Fuel	Coke Gas or oil in the reverberatory	Electricity
Melting Temp.	2550 - 3400^{o}F	2700 - 3200^{o}F
Blowing Temp.	2600 - 3200^{o}F	2800 - 3150^{o}F
Steam	85 - 125 psig	------
Air*	50 - 125 psig	60 - 100 psig
Recovery	35 - 75% by weight of charge	50 - 65%**

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*A spinner arrangement may be used and may be combined with an annular gas nozzle system.

**Percent recovery varies with the individual slags or flyashes and with individual test runs. The numbers reported are the range of averages for four or more test runs on each slag or ash. With industrial equipment and techniques, higher recoveries can reasonably be expected.

Table 18. CHARACTERISTICS OF MINERAL WOOL MADE FROM COAL ASH

		Pouring Temp., °F	Air Pressure, psig	Acid/Base Ratio	Average Fiber Diameter Microns	Fiber Color	Corrosion Retarding Tests	
							Rusting	Etching
Ash	A	3020	95	6.15	7	Light Gray	Very Slight	None
	B	3100	95	10.04	6	White	Very Slight	5%
	C	3000	90	10.01	8	Brown	Slight	5%
	D	3050	90	9.20	6	Light Gray	Less Than Control Strips	5%
	*E	3050	90	1.61	5	White	Slight	None
	F	3100	95	17.8	11	Light Gray	Very Slight	5%
	G	3100	95	14.6	6	Gray	Slight	None
	H	3000	95	14.4	12	Light Buff	Slight	5%
Modified Ash	J	2300	80	1.27	7	Light Brown	Very Slight	None
	K	2600	85	1.00	12	Light Gray	Very Slight	5%
	L	2600	80	1.32	9	White	Very Slight	None
	M	2500	80	1.40	9	Light Gray	Very Slight	5%
	N	3000	100	9.03	14	Gray	Not Tested	Not Tested
Commercial Wool					11	Brown	Less Than Control Strips	10%

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*Lignite Ash

Section 13

BITUMINOUS PAVING MIXTURES

INTRODUCTION

Power plant bottom ash has been utilized in both base and surface courses.[80] In this use, bottom ash is used as a full or partial substitute for conventional aggregates in bituminous mixtures.[81] In order to insure that a particular bottom ash is a potential substitute for a conventional aggregate, the properties of the bottom ash need to be measured. The important properties include: (1) particle size distribution; (2) relative density; (3) soundness. Of these factors, size distribution is considered to be the most important. Soundness is defined as the ability of the aggregate to withstand abrasion and/or crushing.[82] As a general rule, aggregates with a percentage loss equal to or less than 40 percent in the Los Angeles abrasion machine are satisfactory. Durability of the aggregate under freezing and thawing conditions is also very important.[3]

Majidzadeh, et al.[81], has shown that a number of different bottom ashes meet the specifications of conventional aggregates.

ASPHALT MIX DESIGN

The design of an asphalt mix can be based upon one of several methods. The two most widely used techniques are the Marshall and Hveem methods.[81] The Marshall method consists of making specifications of aggregate and bituminous mix by varying the amounts of asphalt. Typical amounts might be 4, 4½, 5, 5½ percent, and so on. Specimens are compacted using a compactive effort applicable to the desired loading conditions. The best mix results when the stability is at a maximum and where the voids between the grains are almost full. After the optimum asphalt content is selected, the specimen must then fulfill a specific design criteria.

TVA INTEREST

During the past two years, TVA has conducted several tests associated with bottom ash. (See Appendix A for specific details of tested samples using the Marshall method.) The Marshall method was used in testing bottom ash from the Watts Bar Steam Plant and the Kingston Steam Plant. The binder used in the tests was an asphalt cement obtained from Volunteer Asphalt Company in Knoxville.

For the Watts Bar samples, the bottom ash was not considered suitable as a base aggregate. For a surface course aggregate, the material larger than the 3/8 inch sieve had to be removed. The optimum blend for asphalt content was estimated at 8.5 percent. This is considered too high to be economical.

For the Kingston Steam Plant samples, the bottom ash was extremely variable in terms of particle size. For a base course, the best asphalt cement content was estimated at between 6.0 and 6.5 percent by weight. The samples could produce a base course that meets all requirements for a Tennessee Department of Transportation grading B, base course.

For surface course tests, the optimum asphalt content is higher than 8.5 percent by weight. Although a surface course material can be made which meets all requirements (with the possible exception of the minimum flow requirement), the necessary asphalt content is too high to be considered economical.

At this time, one test in utilizing ash for road surface aggregate is underway by TVA. A 1.4 mile section of Swan Pond Road near the Kingston Steam Plant has been resurfaced utilizing bottom ash as an aggregate.

The use of bottom ash is a function of economics. With increasing asphalt costs and higher required contents for bottom ash, it appears that bottom ash will continue to be a marginal material except in the case of areas which lack an adequate supply of aggregate.

Section 14

RECOMMENDATIONS

As a result of conducting this study, the authors recommend that the following studies be conducted:

1. Conduct a feasibility study of the conversion of existing wet fly ash collection systems to dry collection and storage. This would lead to better fly ash utilization options within the TVA system.

2. Since some cenospheres do not float, study the mechanical properties of ash to learn how to separate nonfloating cenospheres from ash.

3. As well as proceeding with Mineral Gas Co. in the area of mineral recovery, TVA should compare other process choices and options to see if a preferential process would exist for the TVA region.

4. Conduct an integrated TVA-wide market study for the potential uses, markets, generation points, transportation, and feasibility of extensive coal ash utilization.

Section 15

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Appendix A

Table A-1. FLY ASH TEST DATA*

	RS-413	RS-414	RS-415	RS-416
Steam Plant	Gallatin	Gallatin	Gallatin	Gallatin
Unit No.	#1	#2	#3	#4
Date	3-13-78	3-13-78	3-13-78	3-13-78
Physical Properties				
Specific gravity	2.43	2.43	2.33	2.40
Available alkali, %	--	--	--	--
% passing 325 sieve (wet)	86.1	85.0	75.2	89.4
Loss on ignition, %	1.60	1.55	1.69	3.56
Pozz. index with cement, %	83	77	74	88
Pozz. index with lime, psi	1008	955	939	955
Water Requirement, %	95	96	98	94
Multiple Factor, % (LOIx325 % retained)	22.2	23.3	41.9	37.7
pH of fly ash	11.60	11.50	11.60	11.40
pH of mortar	12.00	12.25	12.25	12.25
Blaine fineness, cm^2/cm^3	8011	6721	7036	3251
Job Sand Mortar Data				
% cement by volume	11.43	11.47	11.40	11.57
% fly ash by volume	8.89	8.92	9.25	9.11
Flow at 15 drops	136	129	135	133
Water/cement ratio	.615	.629	.643	.522
% entrained air	10.67	10.12	10.68	9.61
Compressive strength, psi				
3 day	2962	2771	2580	--
7 day	3973	3790	3568	3997
28 day	6099	5271	5621	6417
90 day	8694	8556	8222	9352
Percent of control				
3 day	127	119	111	--
7 day	128	122	115	129
28 day	144	126	133	152
90 day	174	171	165	187
Chemical Properties				
Silicon Dioxide, SiO_2,%	49.45	49.87	49.68	50.72
Calcium oxide, CaO,%	5.80	5.45	5.00	5.38
Ferric oxide, Fe_2O_3,%	14.90	15.40	15.40	15.40
Aluminum oxide, Al_2O_3,%	19.48	18.80	18.35	18.35
Magnesium oxide, MgO,%	0.98	1.02	1.02	1.05
Sulphur trioxide, SO_3,%	1.42	1.57	1.58	1.54
Moisture content,%	0.37	0.32	0.29	0.28

Table A-1 (continued)

	RS-413	RS-414	RS-41	RS-416
Steam Plant	Gallatin	Gallatin	Gallatin	Gallatin
Unit No.	#1	#2	#3	#4
Date	3-13-78	3-13-78	3-13-78	3-13-78
CL, ppm	52.0	60.0	46.0	60.0
NO_3, ppm	0.4	0.5	0.4	0.3
Cement Properties				
Brand and type	Marquette type II			
C_3A,%	4.50			
Specific gravity	3.15			
Blaine fineness, cm^2/gm	4171			

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[*] Tennessee Valley Authority - Singleton Materials Engineering Laboratory

Appendix B

REPORT ON ASPHALT MIX DESIGN

By A.B. Moore

FINAL REPORT

Prepared by
A.B. Moore, Consultant

February 24, 1977

Subject: Bituminous Mix Design Utilizing Bottom Ash from Kingston Steam Plant.

I. Introduction:

This report presents the results of laboratory testing to determine the mix design and optimum asphalt content utilizing aggregate obtained from the Kingston Steam Plant. Two aggregate gradings were investigated. The first grading utilizes a sample of material conforming to the gradation requirements of the TDOT, Grading B for base courses. The second grading evaluated was obtained by scalping the material above the 3/8 in. sieve from the first grading. This sample conforms to the TDOT, Grading D for surface courses.

II. Materials:

The binder used in these tests was an asphalt cement obtained from Volunteer Asphalt Company. The viscosity grading was AC-20, and the specific gravity was 1.000.

The table below presents the gradations of both fractions included in the tests. The sieve analysis was performed in the TVA labs.

Sieve Size	% Passing, D	Specifications	% Passing, B	Specification
1-1/2	100.0	100.0	100.0	100.0
1	100.0	100.0	94.5	-
3/4	100.0	100.0	86.2	65 - 90
1/2	100.0	100.0	73.3	-
3/8	90.6	88 - 100	66.4	-
4	72.1	56 - 80	52.8	30 - 55
8	53.1	40 - 60	38.9	20 - 45
16	-	-	25.9	-
30	23.5	18 - 38	17.2	8 - 25
50	14.9	8 - 26	10.9	-
100	9.2	5 - 15	6.7	1 - 12
200	3.0	2 - 10	3.0	0 - 7

Eff. S.G. (Bulk) for D grading = 2.34 for B grading = 2.42

III. Procedures:

Test procedures were as described in the following ASTM Designations:

D-70, Specific Gravity of Semi-Solid Bituminous Materials
D-1559, Resistance to Plastic Flow of Bituminous Mixtures Using the Marshall Aparatus
D-2726, Bulk Specific Gravity of Compacted Bituminous Mixtures Using Saturated Surface-Dry Specimens

Since the proposed use for these bituminous mixes is on the secondary road system, a 50 blow compactive effort (Traffic Category - Medium) was used in preparing the specimens for test.

IV. Specification Requirements for the Compacted Samples:

Test Property	Surface Mix Min.	Surface Mix Max.	Base Mix Min.	Base Mix Max.
Stability, lbs.	500	-	500	-
Flow, 0.01 in.	8	18	8	18
Percent air voids	3	5	3	8
Percent voids in mineral aggregate	16	-	12	-

V. Test Results:

The results of all tests are summarized in Figures B-1 and B-2. Figure B-1 presents the results of tests on the Base mixture, and Figure B-2 presents the results of tests on the surface mixture.

VI. Discussion of Results:

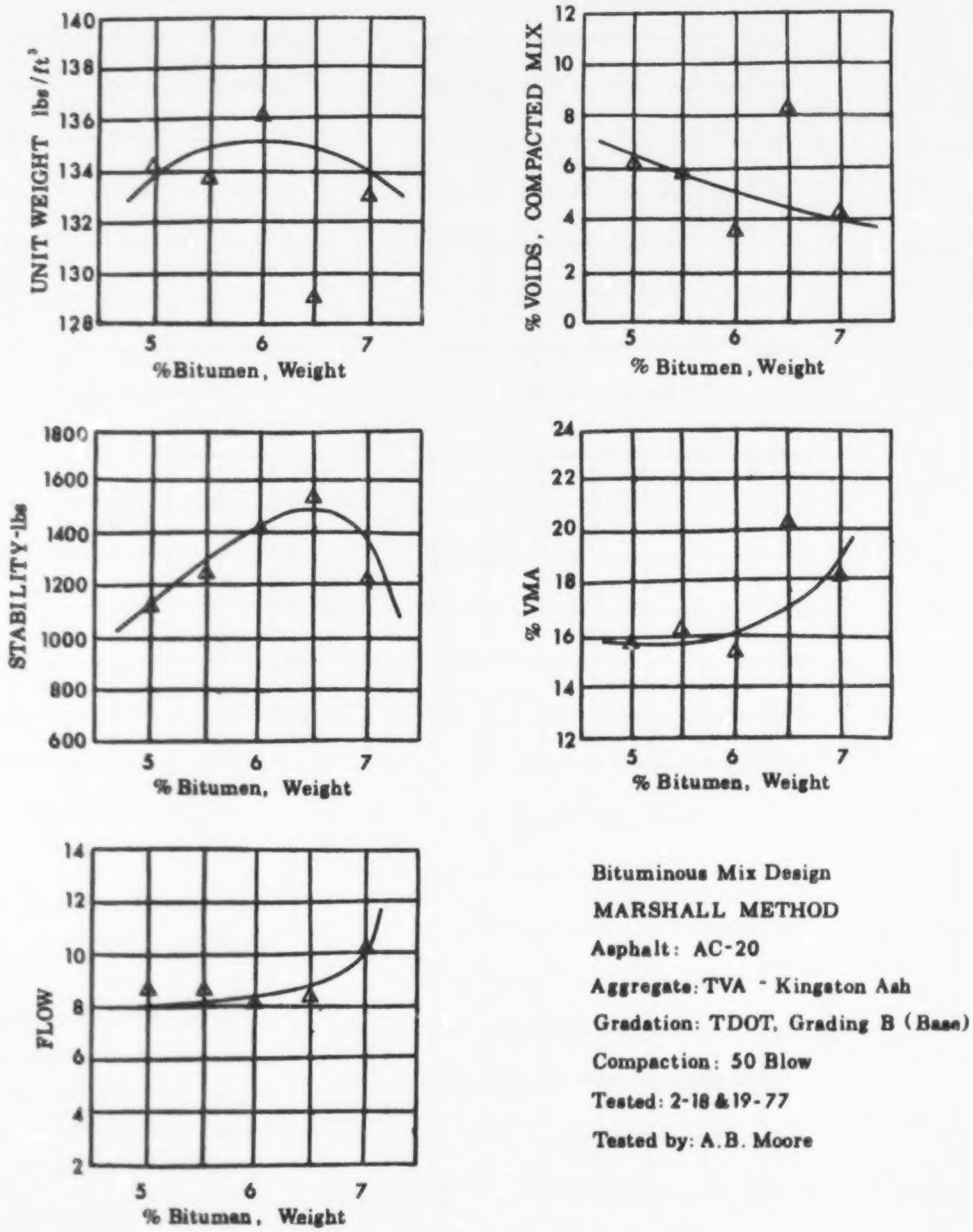
The bottom ash produced by the Kingston Steam Plant is extremely variable. Specific gravity measurements vary with each fraction of particle size as well as within each particle size. The Value measured depends on how much of the expanded clinker type particle and how much of the heavy slag type particle is included in the sample being tested. This variation produced a considerable problem during the Density-Voids analysis phase of the evaluation. Samples with the same asphalt content, by weight, had considerable variation in asphalt content, by volume. The analysis of results was made on a weight as well as a volume basis. However, only the weight basis analysis is presented since the effect of the volume analysis was to shift the plotted points slightly in a lateral direction. No appreciable error in the determination of optimum asphalt content is introduced by using this type of analysis.

1) Grading B, Base Course Analysis:
By referring to Figure B-1, it may be observed that the optimum asphalt content with respect to stability and unit weight appears to be between 6.0 and 6.5 percent asphalt, by weight. The voids curves indicate that an asphalt content of 6.5 percent will provide a percent voids in the compacted mix of approximately 4.5% and a percent voids in the mineral aggregate of approximately 17%. As stated above the voids analysis is subject to question, due to the variable aggregate specific gravities. The flow value in all samples was quite low, even though all samples met the minimum requirement of 8. This is attributed to the highly textured surface of the aggregate particles, which will prevent the particles from moving easily under load. The effect of this low flow value may be to produce a mixture which does not posess a high degree of workability as it is being placed and compacted.

2) Grading D, Surface Course Analysis:
The analysis curves for the surface course mixture, shown in Figure B-2, indicate that an asphalt content as high as 8.5 percent is still below optimum. In designing the experiment it was believed that the finer graded aggregate of the surface course would require a higher asphalt content than the base course aggregate, but the test results indicate that it was even higher than expected. Since this high asphalt content borders on being uneconomical, further testing of samples with higher asphalt contents was regarded as unwarranted at this time. The results which are presented indicate that a surface mixture can be produced from this material that will meet or exceed all requirements with the possible exception of the minimum flow requirement. All samples tested had flow values less than 7, which does not comply with the specification. Again, it appears that the coarse textured particles are concentrated in the finer particle size range, and consequently the lower flow values are appearing in the finer mixtures.

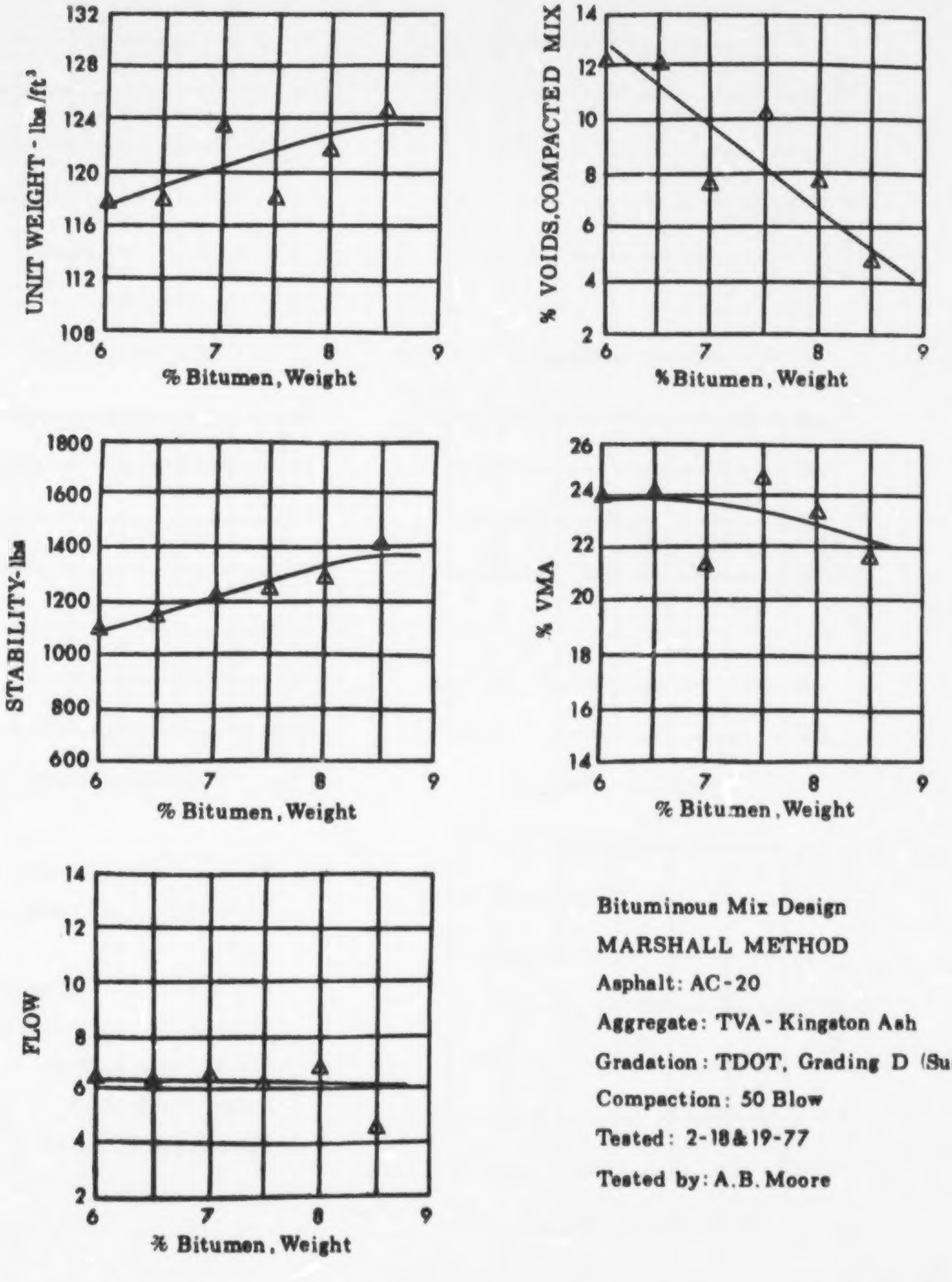
VII. Conclusions and Recommendations:

1) The Kingston Steam Plant ash can be utilized to produce a satisfactory base mixture conforming to the TDOT, Grading B. The asphalt content required to produce the optimum properties is 6.5 percent, by weight.
2) If an emulsified asphalt is used as the binder in the proposed demonstration section, the amount of emulsion to be used will depend on the residue from distillation to indicate the asphalt cement content of the emulsion, which would be equivalent to 6.5 percent, by weight.
3) It is recommended that some type of travel plant be utilized for the mixing of materials rather than a blade type mixing operation. This will insure a more thorough coating action and will reduce segregation.
4) Testing of the ash should also involve a determination of whether an anionic or cationic emulsion should be used as the binder. Some



Bituminous Mix Design
MARSHALL METHOD
Asphalt: AC-20
Aggregate: TVA - Kingston Ash
Gradation: TDOT, Grading B (Base)
Compaction: 50 Blow
Tested: 2-18 & 19-77
Tested by: A.B. Moore

Figure B-1. Bituminous Base Mix Design Using Kingston Ash



Bituminous Mix Design
MARSHALL METHOD
Asphalt: AC-20
Aggregate: TVA - Kingston Ash
Gradation: TDOT, Grading D (Surface)
Compaction: 50 Blow
Tested: 2-18 & 19-77
Tested by: A.B. Moore

Figure B-2. Bituminous Surface Mix Design Using Kingston Ash of the particles resist coating, either from the fly ash dust adhering to the larger particles or due to the presence of other minerals, such as pyrite.

5) Solely on an experimental basis, the B Grading mixture might be used as a surface mix. The gradation does not comply with any of the specified TDOT mixes for surface use, but the other properties of the mix do meet the requirements for a surface mixture. However, two precautions should be taken if it is utilized in a surface mix:
    a) First, the large maximum particle size (1-1/2 in.) will require that the surface layer before compaction should not be less than 2 inches thick and preferably 2-1/4 in. thick.
    b) Second, this mixture is relatively porous, and a fairly heavy tack coat should be used to seal the underlying layers from moisture penetration.
6) Although the D Grading mixture has not been fully evaluated, it could be utilized, again on an experimental basis in the proposed demonstration project, to produce a satisfactory surface mix. The recommended asphalt content for such a mix would be 8.5 to 9.0 percent, by weight. This asphalt content should produce a mix meeting all the requirements with the exception of the flow requirement. However, this high asphalt content will probably not produce a very economical mix. However, due to the low density of the mixture, utilizing this aggregate will provide an increased coverage of approximately 20 percent when compared to a mix utilizing normal weight aggregate. The equivalent asphalt content for a normal weight aggregate mixture would be about 7 percent.
7) Finally, the properties of the mixes utilizing the recommended asphalt contents should be as follows:

Property	Surface Mix	Base Mix
Density, lbs/ft^3	124	135
Stability, lbs	1400	1500
Flow, 0.01 in.	7	9
% Voids, compacted mix	4	4.5
% Voids in the mineral aggregate	22	17

FINAL REPORT

Prepared by
A.B. Moore, Consultant

January 12, 1978

Subject: Bituminous Mix Design Utilizing Bottom Ash from Watts Bar Steam Plant.

I. Introduction:

This report presents results of laboratory testing to determine the mix design parameters and optimum asphalt content utilizing aggregate obtained from the Watts Bar Steam Plant. Tests were conducted using the facilities of the Department of Civil Engineering, The University of Tennessee, Knoxville. Two aggregate gradings were investigated--first, the bottom ash as received from Watts Bar; and second, this same ash after the material retained on the 3/8 inch sieve had been removed. Neither of these fractions were graded to meet a paving specification, but since further aggregate processing would result in additional cost on a commercial basis, it was decided to evaluate the possibilities of the material on an "as received" basis.

II. Materials:

The binder used in the tests was an asphalt cement, AC-20, obtained from the Volunteer Asphalt Company in Knoxville. Lab tests indicate the specific gravity is 1.015.

The table below shows the gradations of both aggregate fractions tested. The sieve analysis and aggregate specific gravities were furnished by TVA. The specification referred to as "D" is that specified by the TDOT for a surface course, and the specification "B" is that specified by the TDOT for a base course material. This information is furnished for comparative purposes, only.

Sieve Size	Spec. "D"	As Received % Passing	Spec. "B"	+3/8 Scalped % Passing
1-1/2	100	100.0	100	100.0
1	100	100.0	-	99.2
3/4	100	100.0	65-90	98.2
1/2	100	100.0	-	95.1
3/8	88-100	95.4	-	90.7
4	56-80	82.0	30-55	78.0
8	40-60	66.5	20-45	63.3
16	-	33.8	-	32.1
30	18-38	18.2	8-25	17.2

(Con't.)

Sieve Size	Spec. "D"	As Received % Passing	Spec. "B"	+3/8 Scalped % Passing
50	8-26	11.2	-	10.6
100	5-15	7.2	1-12	6.8
200	2-10	5.0	0-7	5.0

Effective SG (Bulk): "D" Grading = 2.56 "B" Grading = 2.51

III. Procedures:

Test procedures were as described in the following ASTM Designations;

D-70, Specific Gravity of Semi-Solid Bituminous Materials

D-1559, Resistance to Plastic Flow of Bituminous Mixtures Using the Marshall Apparatus

D-2726, Bulk Specific Gravity of Compacted Bituminous Mixtures Using Saturated Surface-Dry Specimens

Since relatively low stability values were expected, due to the aggregate grading problems, it was decided to use a 75 blow compactive effort in preparing the Marshall samples for test.

IV. Specification Requirements for the Compacted Samples (Medium Traffic):

Test Property	Surface Mix		Base Mix	
	Min.	Max.	Min.	Max.
Stability, lbs.	500	-	500	-
Flow, 0.01 inches	8	18	8	18
Percent air voids	3	5	3	8
Percent voids in min. aggregate	16	-	12	-

V. Sample Preparation:

Three samples were prepared at each asphalt content. Test results reflect the average of three samples, except that one of the 6 percent "B" grading samples was dropped and destroyed prior to testing. The asphalt contents to be investigated were estimated to encompass the optimum for both gradings and were taken at 0.5 percent intervals betweeen the maximum and minimum levels shown below:

Grading "D": 6.5 - 8.5 percent
Grading "B": 5.0 - 7.0 percent

VI. Test Results:

The results of all tests are summarized in Figures B-3 and B-4. Figure B-3 presents the results of the tests conducted on the surface mixture, "D." Figure B-4 presents the results of the tests conducted on the base mix, "B."

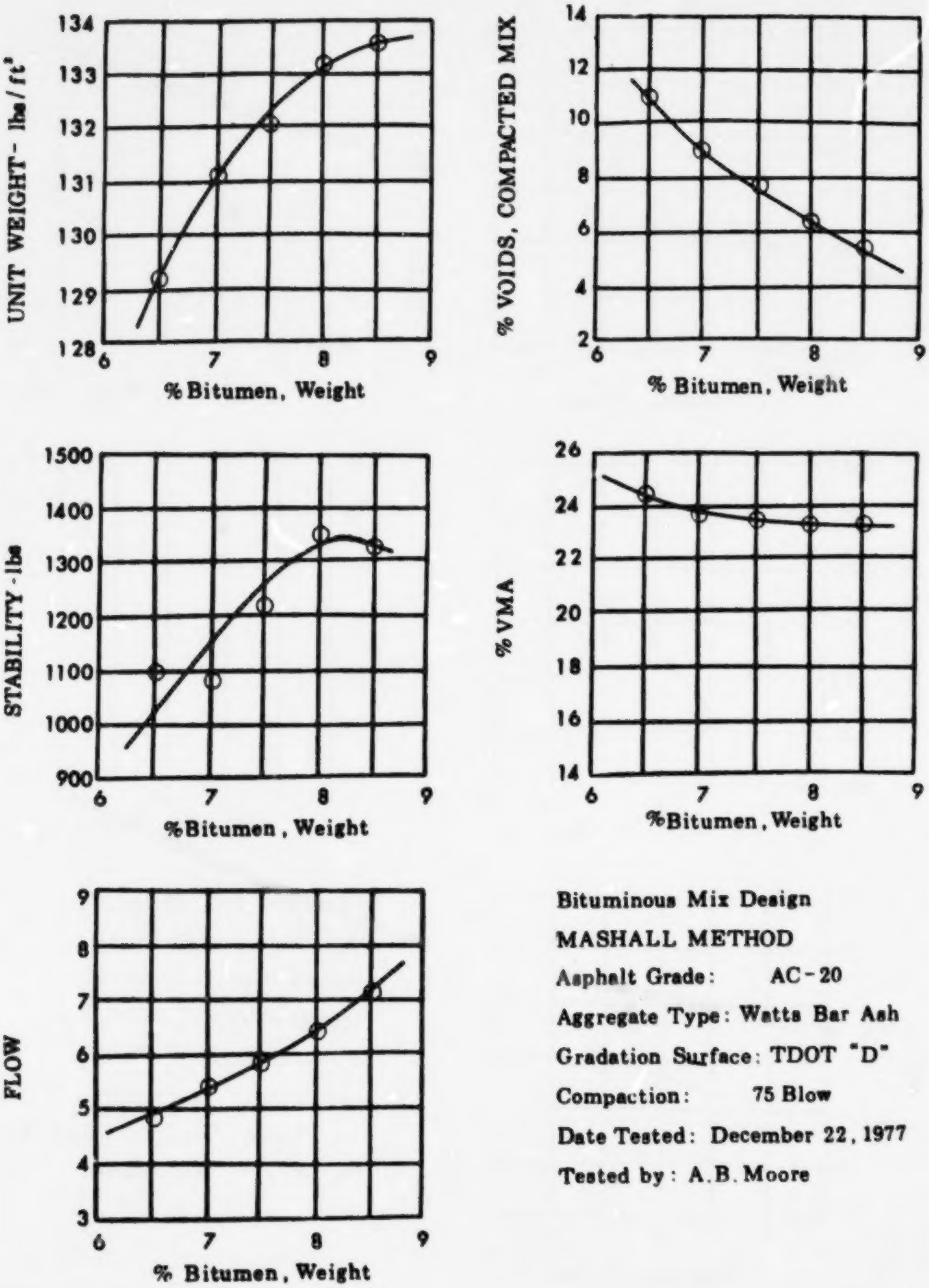
VI. Discussion of Results:

The variations in specific gravity of the Kingston Steam Plant bottom ash, noted in a previous report, were not as severe in the bottom ash obtained from the Watts Bar Steam Plant. Therefore, the density-voids analysis of the Watts Bar material produced somewhat more meaningful results. The major problem with the Watts Bar ash is in the gradation. The surface gradation "D" test results were quite uniform, which is a result of the fact that this gradation varies only slightly from the TDOT specification for a surface aggregate. The results of tests on the base gradation "B" material were quite variable due mainly to the extreme variation from the TDOT specification, particularly in the percent passing the 3/4-in., No. 4 and No. 8 sieve sizes. As noted below, this gradation will not provide a suitable material for a base mix.

1) Grading "D", Surface Course Analysis:
Analysis of the data shown in Figure B-3 indicates that a satisfactory surface mix could be constructed with this material at an asphalt content of 8.5 percent, by weight. This asphalt content would optimize the stability and density of the mix. However, this asphalt content is not sufficient to provide the required voids in the compacted mix. The data indicate a voids content of 5.5 percent, as compared to the required maximum of 5.0 percent. An asphalt content of 9.0 percent would probably produce a mix that would meet all requirements of the specifications. An asphalt content of 8.5 percent does not meet the minimum flow requirement either, but it would produce a mix with a flow of approximately 7 which is only one below the required minimum.

A minor adjustment in the aggregate gradation might be more economical than using this relatively high asphalt content. The addition of aggregate particles in the size range of the No. 4 sieve would have the effect of closing the void structure, which would result in a lowered asphalt content to produce a mixture to meet the specification requirements. Analysis of this possibility was not an objective of this investigation.

2) Grading "B", Base Course Analysis:
The normal range of asphalt content in a base mixture is 3-5 percent. Test results, shown in Figure B-4, indicate the optimum asphalt content for this aggregate gradation is in excess of 7.0 percent. An asphalt content of 7.0 percent produces a mix with the following properties: unit weight - 128.4 lbs/ft^3, stability -



Bituminous Mix Design

MASHALL METHOD

Asphalt Grade: AC-20

Aggregate Type: Watts Bar Ash

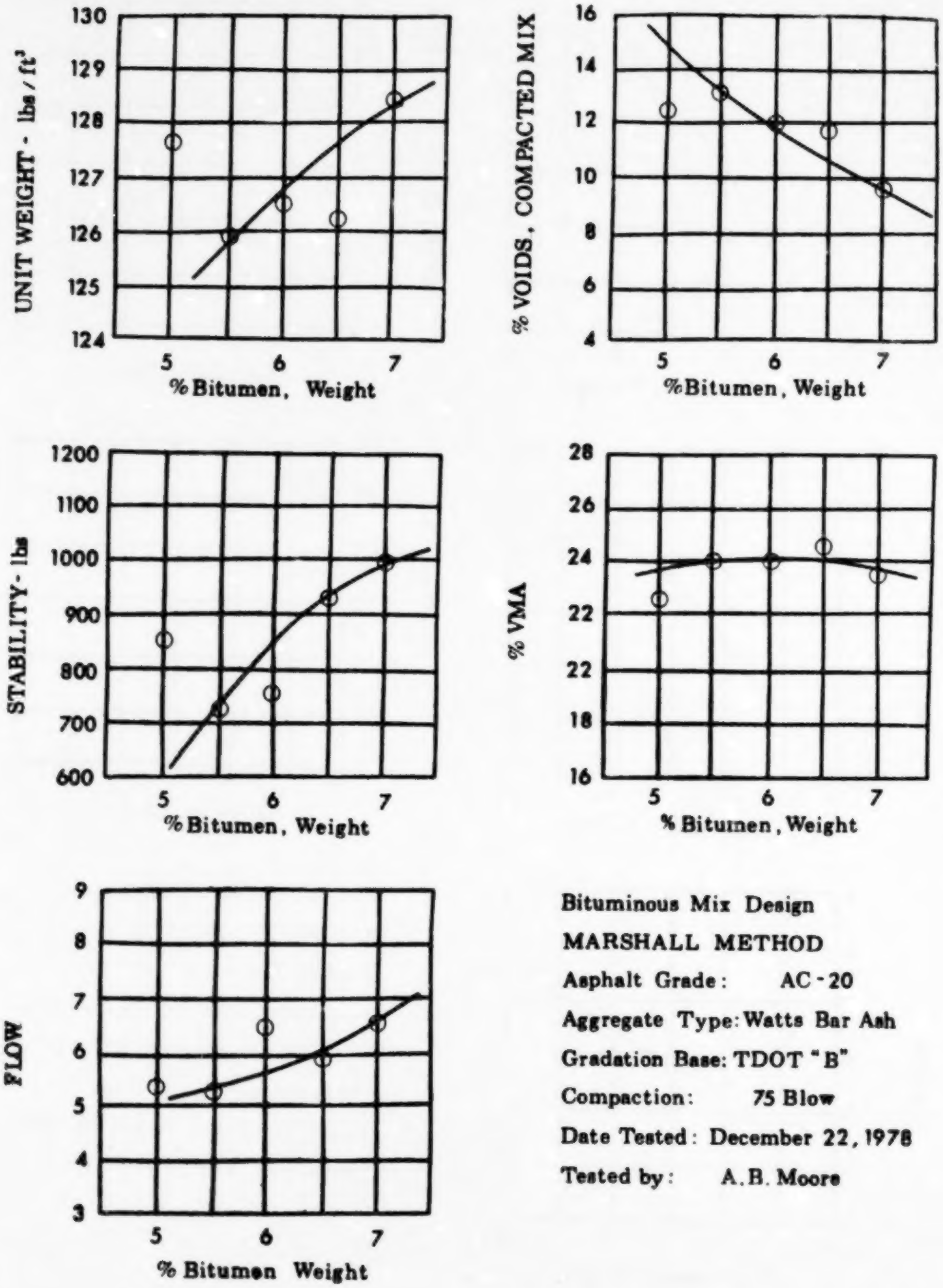
Gradation Surface: TDOT "D"

Compaction: 75 Blow

Date Tested: December 22, 1977

Tested by: A.B. Moore

Figure B-3. Bituminous Surface Mix Design Using Watts Bar Ash



Bituminous Mix Design

MARSHALL METHOD

Asphalt Grade: AC-20

Aggregate Type: Watts Bar Ash

Gradation Base: TDOT "B"

Compaction: 75 Blow

Date Tested: December 22, 1978

Tested by: A.B. Moore

Figure B-4. Bituminous Base Mix Design Using Watts Bar Ash

990 lbs., flow - 6.5 and voids - 9.5 percent. These values indicate that an economical mix cannot be produced using this aggregate gradation. The major problem with this mixture may be observed by referring to the table on page 1 of this report. This gradation is excessively different from the requirement of the following sieves; 3/4 in., No. 4 and No. 8.

VII. Conclusions and Recommendations:

1) The Watts Bar bottom ash may produce a satisfactory surface aggregate after the material larger than the 3/8 inch sieve is removed. However, the high asphalt content (8.5 percent) required to produce an optimum mixture may not be economical.
2) The voids in the compacted mix at an 8.5 percent asphalt content surface mixture would be approximately 5.5 percent, which exceeds the required maximum of 5.0 percent. However, it is my opinion that this would not have a large adverse effect on the durability of the mix.
3) The Watts Bar bottom ash, as received, will not produce a satisfactory base aggregate.

Appendix C

"Fly Ash Concrete Mix Design Procedures"

PRINCIPAL METHODS USED TO DETERMINE MIX RATIOS

Cannon has stated that many concrete mix designers substitute fly ash for cement on a one-for-one basis either by volume or weight.[59] Most fly ash concretes developed with this mix proportioning will usually have a compressive strength greater than a comparable all cement portioned concrete at ages beyond 90 days. However, the compressive strength between 3 to 28 days for the fly ash concrete is usually lower than that of a comparable non-fly ash concrete. Because of this difference in strengths at early ages, many have concluded in the past that fly ash concrete should be used only where strength is not the principal requirement.

Several different mix design methods have been developed for fly ash concrete where comparable strengths are assured between fly ash concrete and a typical Portland Cement concrete.[59] Lovewell and Washa have developed a procedure for proportioning fly ash in a concrete mix which results in approximately equal compressive strength during the period of 3 to 28 days.[58] Their proportioning method is based on the mixture of flyash and Portland Cement having a total weight greater than the cement used in a comparable straight Portland Cement.

Cannon has also developed a mix design based upon a number of investigations at TVA.[59] His approach is readily adaptable to different qualities of fly ash as well as meeting standards for Type I or Type II cement. This design approach is as follows:

STEP 1: Select the volume of coarse aggregate per unit volume of concrete from Table 6 of ACI 613-54.[52] In making this selection the fineness modulus of the sand should be reduced by 20% to allow for the effect of the larger volume of the cementitious material in the fly ash mix.

STEP 2: Estimate the water requirements for the maximum size of aggregate to be used and the required slump (use ACI-613-54 as a guide).[52] Slump is a measure of workability and represents the distance that an unsupported cone of concrete will settle in height below the form used to form the cone of concrete.

STEP 3: Select from Figure C-1 the water-cement ratio required for a given strength concrete.

STEP 4: Select the fly ash proportion to be used by either Figure C-2 or Figure C-3. The selection is based on the relative cost of fly ash and required strength in order to select the lowest cost blend of fly ash and cement.

STEP 5: Using the water-cement ratio of step 3 and fly ash proportion of step 4, determine the water reduction from Figure C-4 or Figure C-5.

STEP 6: Using the estimated water requirements of step 2 for the control mix, determine the water requirements of the fly ash mix by using the water reduction of step 5.

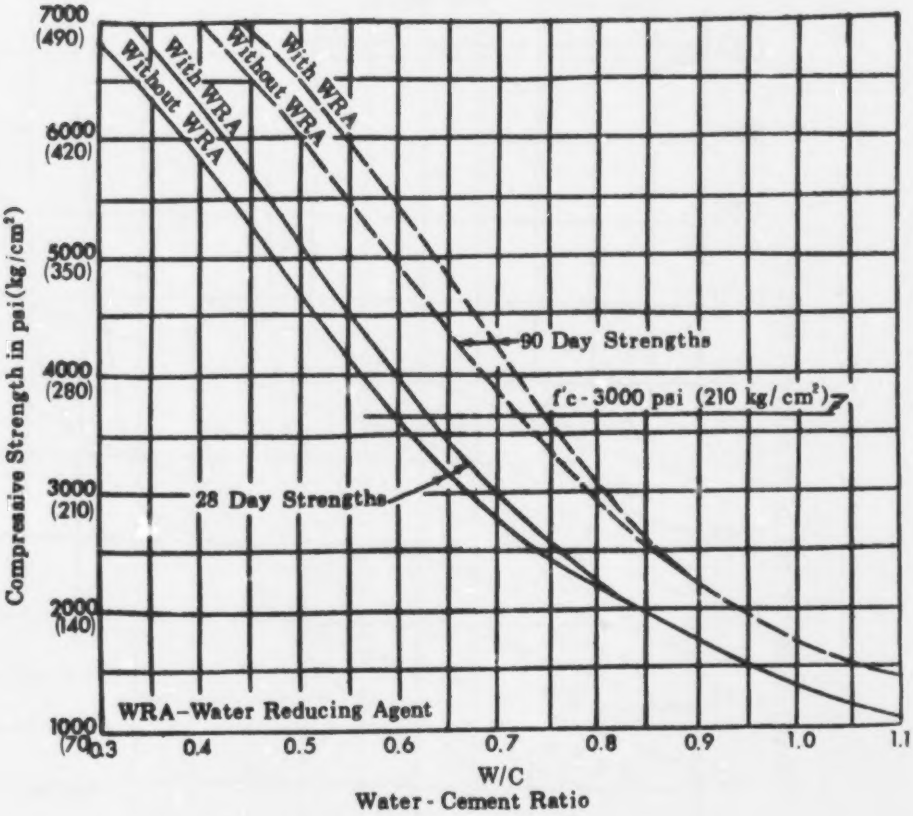


Figure C-1. Water-Cement Ratios and Compressive Strengths

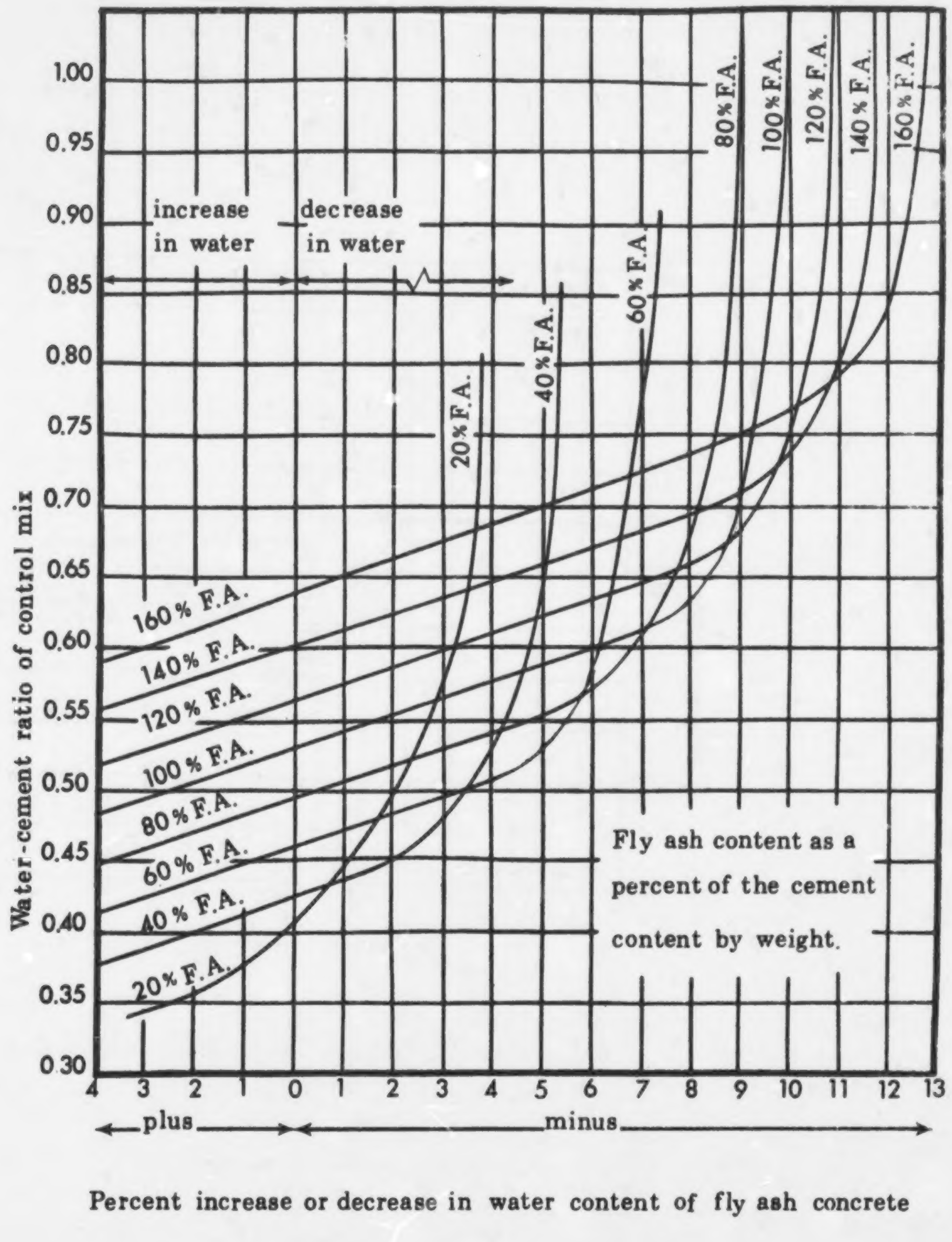


Figure C-2. Comparison of Water Requirements of Concrete With and Without Fly Ash for Identical Slump, Air contents and 28 Day Strength

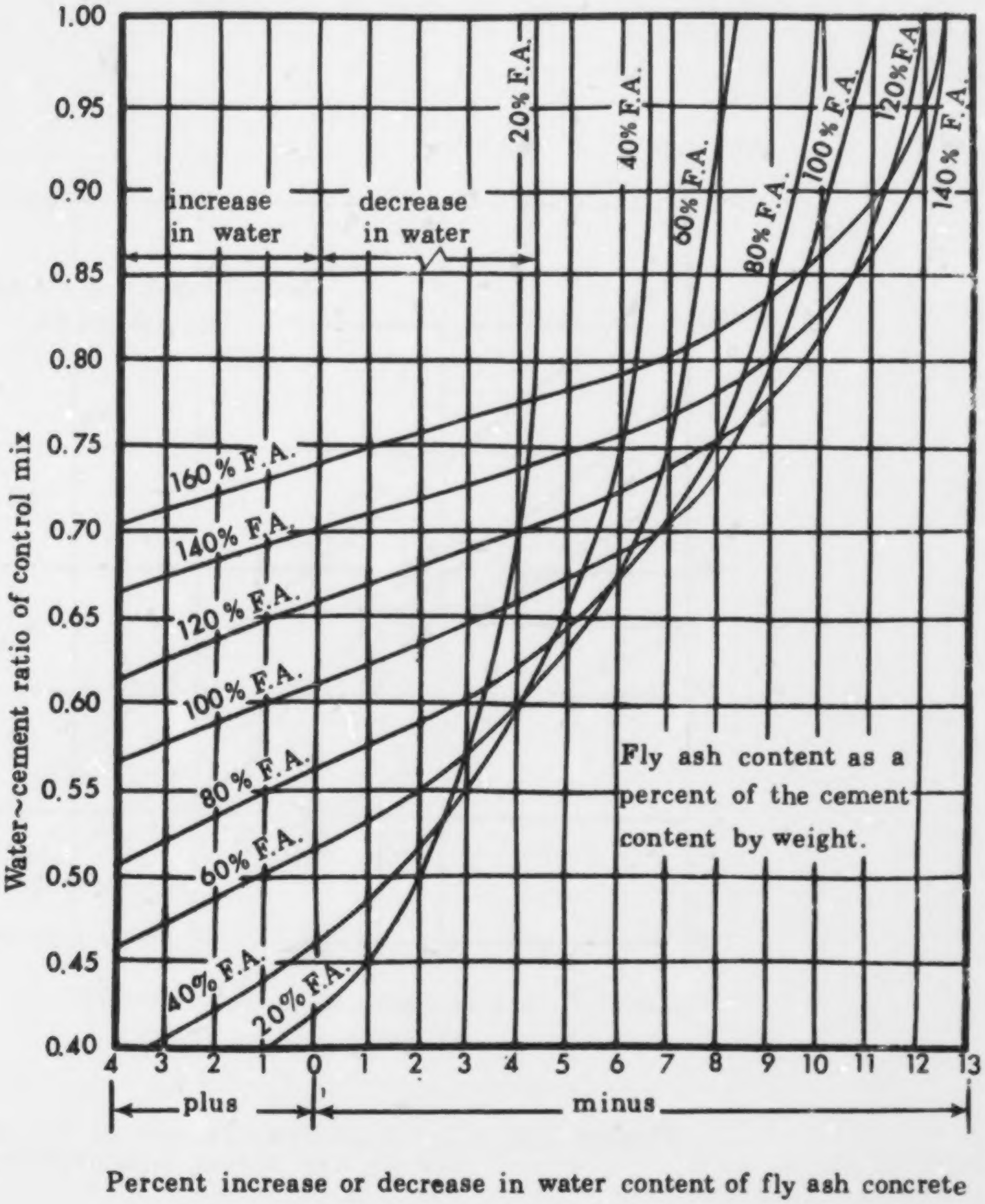


Figure C-3. Comparison of Water Requirements of Concrete With and Without Fly Ash for Identical Slump, Air Contents and 90 Day Strength

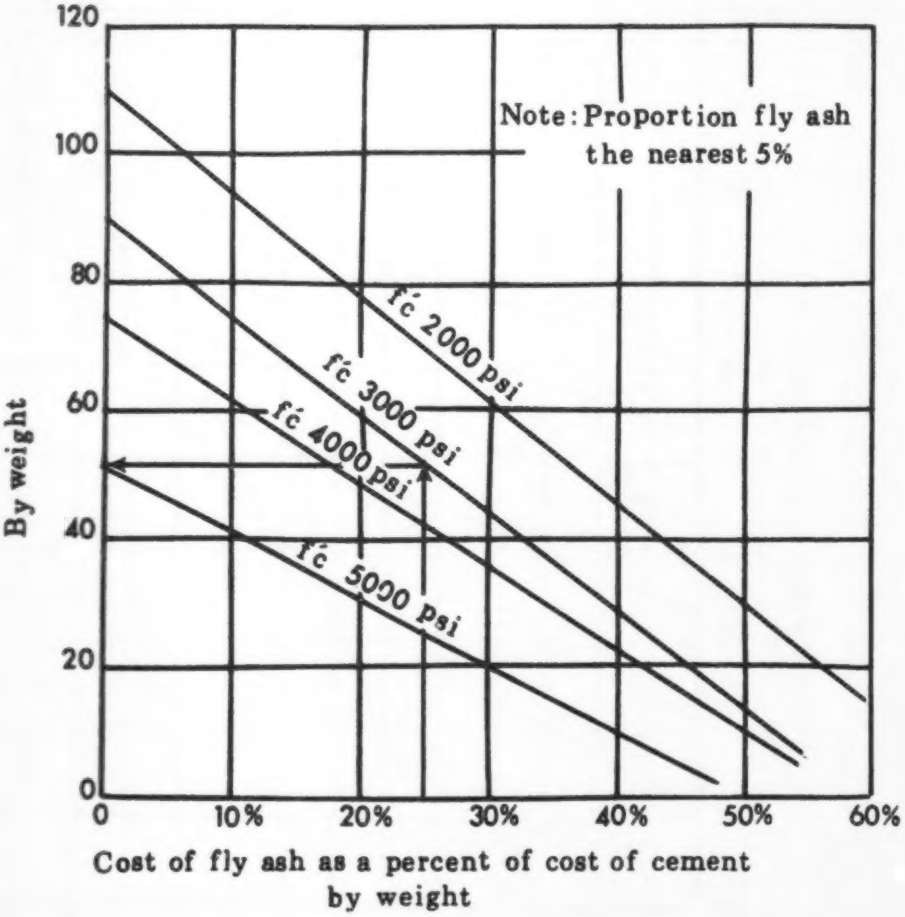


Figure C-4. Economic Proportions of Fly Ash for 28 Day Strength Concrete

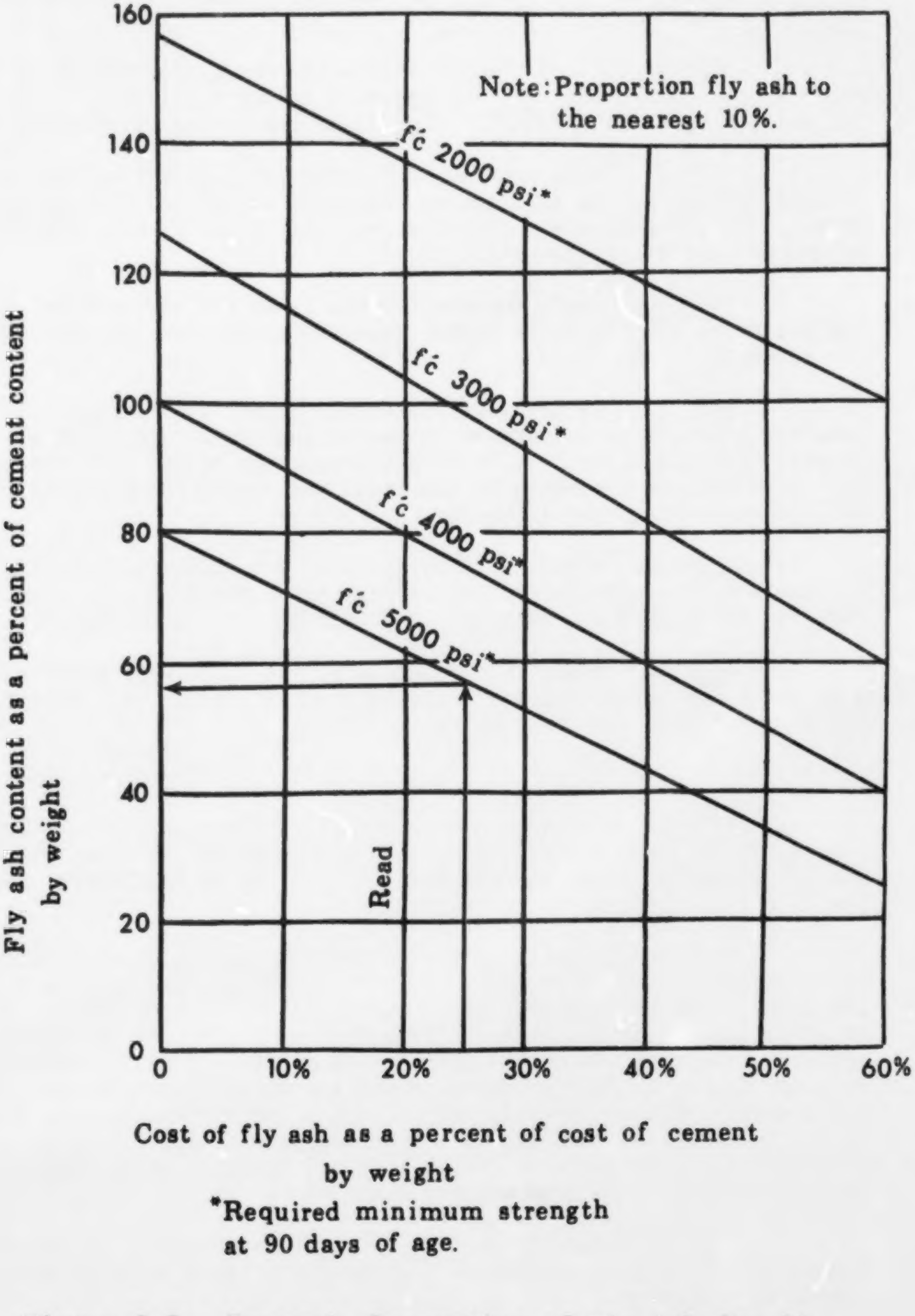


Figure C-5. Economic Properties of Fly Ash for 90 Day Strength Concrete

STEP 7: Determine the cement requirements of the control mix by dividing the control mix water requirements by the water-cement ratio of step 3.

STEP 8: Select the proportionate cement requirement of the fly ash mix from Figure C-6 or C-7 (depending on the age strength requirements) using the water-cement ratio of step 3 and the fly ash proportion of step 4.

STEP 9: Using methods in ACI-613-54[52], determine the solid volume of sand for the mix by subtracting the solid volumes of coarse aggregate, cement, fly ash and water, plus the required volume of air from the unit volume of concrete in the mix.

STEP 10: Check the mix for the slump and air content and repeat the procedure for the actual water required to provide the desired slump and air contents.

STEP 11: If trial mix strengths differ significantly from the required strength an adjustment in cement and fly ash contents will be required. This adjustment is in direct proportion to the water-cement ratio of Figure C-1 corresponding to the trial mix strength divided by the original water-cement ratio used in design.

Let us assume we wanted to design a 28 day, 3000-psi concrete with 1½ in. maximum size aggregate, five percent air content, 2½ in. slump, no water reducing agent, and fly ash cost at 25 percent of cement cost.*

STEP 1: Using Table 6 of ACI-613-54[52] and a fineness modulus of 2.6, the volume of aggregate to volume of concrete is .74. If the aggregate has a specific gravity of 1.6 then

$$.74 \times 27\ \mathrm{ft}^3/\mathrm{yd} \times 1.6 \times 62.5\ \mathrm{lb}/\mathrm{ft}^3 = 2000\ \text{lbs. of aggregate}$$

STEP 2: With an air entrainment of 5 percent, and an aggregate size of 1½ in., one can see from Table 3 of ACI-613-54[52] that between 29 and 32 gallons of water are required for a slump of 2.5 inches. We will use 30 gallons or 250 lbs. of water.

STEP 3: Concrete is tested for compressive strength according to ASTM specifications. For each 150 yd^3 of concrete, two to 3 test cylinders are made. From the compressive strengths of the test cylinders, a coefficient of variation can be determined. From the coefficient of variation, and a specification that the design strength be met in a certain percentage of cylinder tests, a required strength for a mix can be determined. For example, for a coefficient of variation of 15% and no more than one weak test cylinder in 10, the required strength to design strength is 1.23.[50] Thus, the required strength of the concrete is 3000 x 1.25 = 3700 psi. Using Figure C-1 the water-cement ratio for a 28 day strength 3700 psi is .59.

STEP 4: From Figure C-4, and a fly ash cost of 25 percent of the cement cost, the most economical mix would utilize a ratio of fly ash to cement of 50 percent.

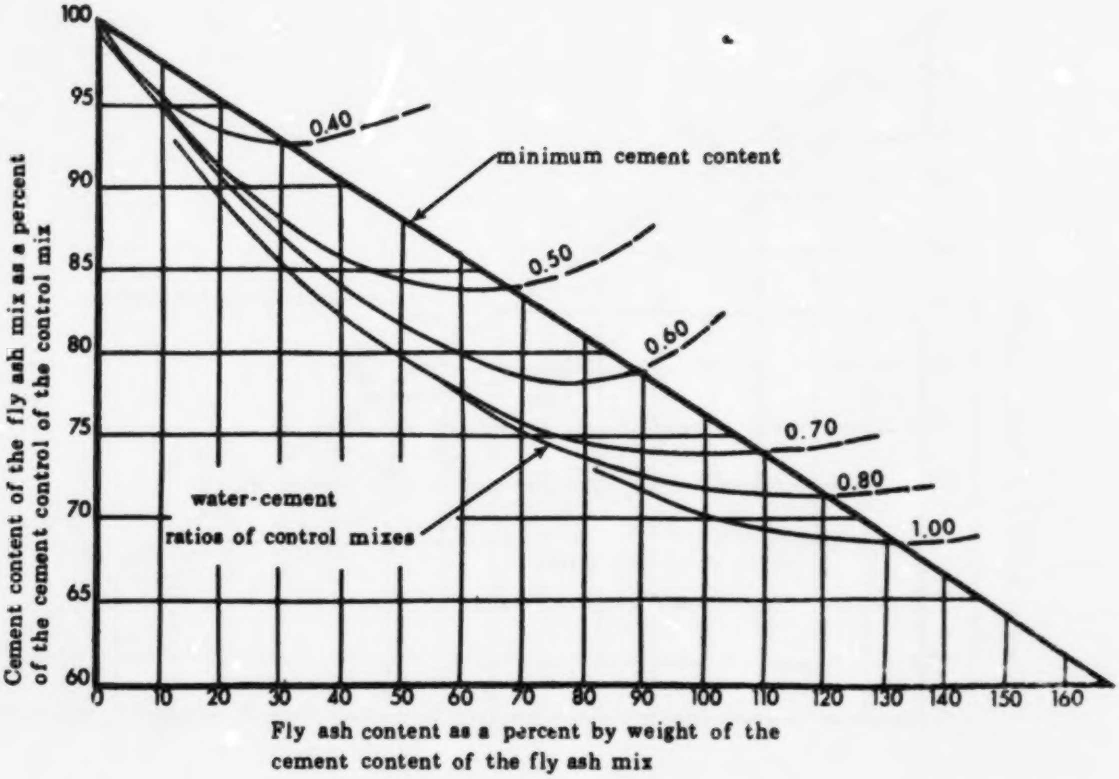


Figure C-6. Cement Requirements for Various Fly Ash Proportioned Concretes for 28 Day Strength

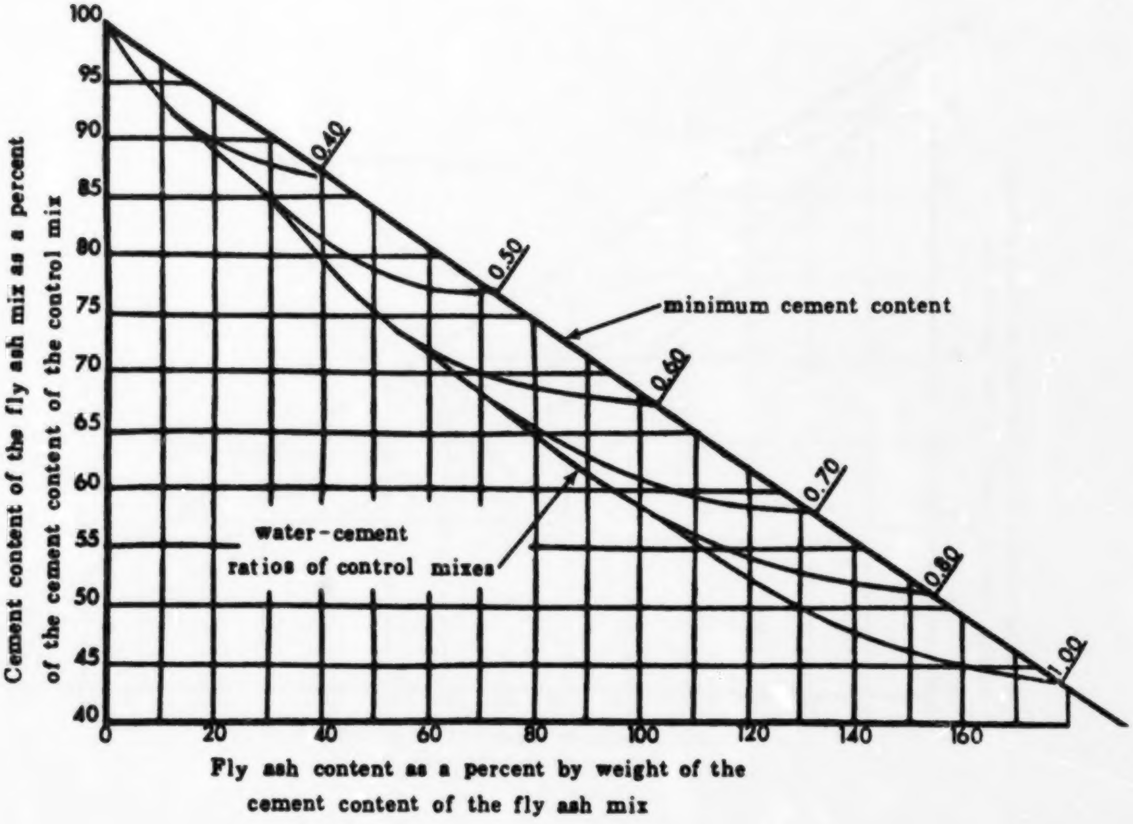


Figure C-7. Cement Requirements for Various Fly Ash Proportioned Concretes for 90 Day Strength

STEP 5: From Figure C-2, a fly ash to cement ratio of .5 by weight and a water-cement ratio of .59, the water reduction should be about 4%.

STEP 6: The water content of the fly ash concrete is less than 250 lbs (.96) = 240 lbs.

STEP 7: Since the water-cement ratio is $w/C_m = .59$ and the water content is 240 lbs, then the control mix concrete has

$$cm = \frac{w}{w/C_m} = \frac{250}{.59} = 425 \text{ lbs. of cement}$$

STEP 8: From Figure C-6, the fly ash mix cement content equals 80 percent of the cement content of the control mix when the water-cement ratio is 50 percent. This means that the cement in the fly ash concrete equals:

.80 x 425 = 340 lbs. of cement

STEP 9: We need to calculate the volume of sand given the specific of 2.65 for sand.

Ingredient	Weight (lbs.)	Volume (cu.ft.)
Aggregate	2000	12
Cement	340	1.71
Fly ash	170	1.14
Water	240	3.84
Air (5%)	-	1.35
Subtotal	-	20.04
Sand needed	1149	6.94
Total	3899	27

STEP 10: Assume slump is within ±¼ in. of design slump.

STEP 11: Assume trial mix had an average 28 day strength of .3750 psi., then no adjustment is necessary.

After calculating a total for flyash and cement contents, it is easy to calculate the overall economics of the fly ash concrete as opposed to an all-cement cost without the cost of aggregates. The comparisons are given in Table C-1. The above analysis is made without adjusting for the cost of equipment needed for fly ash handling equipment. This will be discussed further in the economics of fly ash. In addition, the use of any admixtures for keeping air entrainment at suitable levels is not included here but will be discussed later.

EFFECT OF FLY ASH ON WATER CONTENT

It is generally agreed that the use of fly ash in limited amounts as a

TABLE C-1. ECONOMICS OF FLY-ASH MIX

	Fly Ash Mix					
Ingredient	Weight lbs.	Cost Unit	Total	Weight lbs.	Cost Unit	Total
Cement	340	$47/2000	7.99	373	$47/2000	8.77
Fly Ash	170	$10/2000	.85	-	-	-
Water	240	-	-	250	-	-
Added Sand	0	-	-	100	$2/2000	.10
Total			8.84			8.84

replacement for cement or as an addition to the cement, or in replacement of some sand, does not appreciably affect the water requirement for maintenance of the same slump. Slump is a measure of workability and represents the distance that an unsupported cone of concrete will settle in height below the form used to form the cone of concrete.[54] Although the water needed for a given slump and maximum size aggregate remains relatively unchanged when fly ash is included, some controversy still exists as to the water requirement when the fly ash is coarse and has a high carbon content.[61]

The water-to-cement ratio has a great influence on the overall strength of concrete. Since the workability is a function of aggregate size and water content, it is necessary to determine a water requirement based on aggregate size and desired workability and then translate the water requirement to a cement content based on a design strength.[56] After the cement content and fly ash content are calculated, it is important to recalculate the needed water as done in the Cannon mix method.[59]

REDUCTION IN CEMENT CONTENT

The reduction in cement content must be based on the relative costs of cement and fly ash and the design compressive strength. Figure C-4 gives the relationship between the fly ash to cement ratio and the ratio of fly ash to cement cost as a function of the 28-day design compressive strength. For example, for a fly ash-to-cement cost ratio of .36 and a design strength of 3000 lbs. per square inch, the fly ash-to-cement ratio (by weight) is 34 percent. This gives us the economical ratio of amounts in the fly ash concrete. The reduction in cement is based on the ratio of a fly ash to cement ratio and the water-cement ratio needed for desired workability and aggregate size. This relationship is given in Figure C-6. For example, if the weight ratio of fly ash to cement is 34 percent and the water to cement ratio was .5, then the cement in the fly ash mix would be 85 percent of the amount in a non fly ash mix. This would represent a reduction of 15%.